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EXCITON OPERATORS - COMMUTATION RELATIONS AND DYNAMICS

BY

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A Dissertation submitted to the Graduate School
in partial fulfillment of the requirements
for the Degree

Master of Science

Major Subject: Physics

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August 1997

" Exciton Operators - Commutation Relations and Dynamics ," a dissertation prepared by Delene J. Nelson in partial fulfillment of the requirements for the degree, Master of Science , has been approved and accepted by the following:

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ACKNOWLEDGMENTS

Thanks to my supervisor Dr. Margaret Hawton for her patience, guidance and support. This document would not exist without her.

Thanks to all the members of the Lakehead University Physics department for their warm acceptance, support and dedication.

Thanks to Lakehead University and the philosophy department. The opportunities for learning that I have experienced in this facility have been beyond any expectations. Thanks also to the university for their financial support.

Thanks to NSERC for their generous financial support.

Thanks to family and friends who have supported me and inspired me along the way.

Most of all thanks to Charlie for picking me up when I was down and keeping me grounded when I was up, this would not have been possible without you.

ABSTRACT

EXCITON OPERATORS - COMMUTATION RELATIONS AND DYNAMICS

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The electron-hole pair operator commutation relations for a semiconductor are explicitly derived showing that the pairs are quasi-bosons with statistics intermediate between bosons and fermions. These pair operators are transformed into exciton operators, that incorporate the intra-pair Coulomb interaction, and it is found that the commutation relations remain quasi-bosonic. The exciton dynamics written in terms of the exciton operators are derived in the Heisenberg picture and compared with the traditionally used semiconductor Bloch equations.

Contents

Chapter 1

Introduction

Excitons have been studied since the 1930's. There are two types of excitons, the tightly bound Frenkel exciton and weakly bound Wannier exciton. The Wannier exciton is found in semiconductors and is the type of exciton this thesis will deal with. Traditionally Wannier excitons have been treated as Bosons to a first approximation. This turns out to be a good approximation when there is a low density of excitons. However it is now possible, due to the high intensity lasers that are now more readily available, to easily create systems with high densities of excitons . These high density systems lead to observed [1] deviations from boson statistics for excitons. Consequently, it is necessary to understand the nature of the exciton a little better.

Experiments with Cu_2O have reignited the discussion as to whether Bose condensation will occur for excitons [2]. This, combined with the suggestion that no Bose condensation will occur for ideal gases with fractional exclusion statistics [3], seems again to suggest that a closer look at the commutation relation of the exciton is justified.

In his 1960 paper Usui, [4] used operators to deal with the electron gas model.

The operators used approximated excitations as bosons. Usui pointed out that this approximation, which was first made in 1957 by Sawada [5] and Wentzel [6], greatly simplified the calculations involved in the electron gas problem and seemed to give results that coincided with the Hartree-Fock treatment. Usui, however, does not explicitly work out the commutation relations. This treatment of the exciton as bosons led to question of whether the boson property of condensation could be seen for excitons. Hanamura and Haug [7], in their 1976 summary paper on condensation effects of excitons, take the fermionic expression of the exciton and express it in terms of pair operators which they determine are bosons with a correction factor that is small provided the average distance between the excitons is much larger than the average size of the exciton. They then use Usui's transformation to describe the exciton Hamiltonian in terms of the exciton operators. Haug and Koch [8] put forward the idea of exciton operators, that are approximately bosonic, but do not transform the pair operators into exciton operators and do not use these exciton operators in their Hamiltonian. Consequently, in deriving the dynamics of the exciton, the electron and hole are treated separately and the Coulomb interaction between the electron and the hole must be included explicitly in the Hamiltonian. The semiconductor Bloch equation's state filling is still fermionic due to this use of electron and hole operators. Bassani *et al* [9] also use pair operators, with the assumption that they are bosonic at low densities, to derive the Hamiltonian of the excitons interacting with an electromagnetic

field. Jacobson *et al* [1], on finding deviations from Bose statistics for excitons at higher excitations, propose a commutation relation that explicitly describes the deviation from Bose statistics. However, this new commutation relation is not explicitly derived and is a simple form of the commutation relations that will be derived in this thesis. This commutation relation that is proposed in Jacobson *et al* [1], like our commutation relation does not agree with the commutation relations that have been derived [10] for particles with small violation of Fermi or Bose statistics, often called quons.

This thesis is divided into two parts. The first part will explain the band structure of a semiconductor leading to a description of the conduction band electrons and valance band holes. This allows for the modelling of the exciton in a semiconductor. The distinctions between fermions and bosons will be explicitly described. The commutation relations are then derived in terms of the electron and hole operators, clearly showing that excitons are not bosonic but rather intermediate between fermions and bosons. This result will be transformed into the commutation relations in terms of exciton operators through the use of Usui's [4] transformation.

The second part of the thesis deals with exciton dynamics. The dynamics of the exciton are traditionally described by the semiconductor Bloch equations. However the derivation of these equations still treats the electron and hole as a pair not as a bound entity or exciton. The semiconductor Bloch equations also

require the random phase approximation or Hartree-Fock approximation, which is ill-controlled. The result is that the range of validity of the semiconductor Bloch equations is not clearly understood [11].

The second part of the thesis will also develop the physics of the excitons leading to the Hamiltonian, including coupling with the electromagnetic field. The transformation of the Hamiltonian will then allow it to be expressed in terms of the exciton operators. The exciton dynamics in the Heisenberg picture are then compared with the semiconductor Bloch equations.

The conclusion section will give a summary of the findings and a discussion of how this approach can be of benefit to the understanding of excitons, and the explanation of the results of future experiments. The possibilities for future studies will also be discussed.

Part I

Commutation Relations.

Chapter 2

The Exciton in a Semiconductor.

Band Theory

The free electron model, which describes properties of a crystal through the assumption that the valence electrons are essentially free, is successful at describing many of the properties of metals but fails to help distinguish metals from semiconductors. If we think of all crystals, semiconductors or otherwise, as being created from free atoms brought close together, then it seems logical to assume that the discrete energy level of the atom would somehow be reflected in the solid. In fact, while crystals may have characteristic optical spectra which demonstrate sharp resonance-like structures, a lot like atomic spectra, they also have other electronic properties, e.g. insulators versus conductors, that are best explained in terms of energy bands. These bands can be thought of as being derived from the discrete energy states of the atom. The free electron model does not allow for the formation of energy bands.

To allow for the bands we cannot neglect the periodic lattice of the solid. Thus the Bloch theorem and the $\mathbf{k} \cdot \mathbf{p}$ model [8] will be used to explain band theory. This theory then allows for the description of electrons in the conduction band

and holes in the valance band giving rise to excitons.

Bloch Theorem.

Consider an ideal crystal for a moment. The ideal crystal is an array of atoms periodically spaced from each other, there are no flaws in the lattice and there are no impurities present. The ideal crystal needs to be infinite so that boundary conditions are not a consideration. If we now consider that each of the atoms has at least one valence electron which is less tightly bound than the inner electrons (the electrons in closed shells), we can then treat the nucleus and the inner electrons as a positive ion and the valence electrons as nearly free electrons.

The array of ions will therefore affect a positive, periodic potential on the valence electrons which satisfies

$$V_o(\mathbf{r}) = V_o(\mathbf{r} + \mathbf{R}_n) \tag{2.1}$$

where $\mathbf{R}_n$ is a lattice vector joining two equivalent sites,

$$\mathbf{R}_m = \sum_i m_i \mathbf{a}_i. \tag{2.2}$$

Here m_i are integers and $\mathbf{a}_i$ are the basis vectors that span the unit cell of the lattice. In general there can be more than one atom per unit cell.

The Hamiltonian for one of the valence electrons in the periodic potential is

$$H = \frac{p^2}{2m_e} + V_o(\mathbf{r}) \tag{2.3}$$

where m_e is the free electron mass and

$$H\Psi_n(\mathbf{r}) = E_n\Psi_n(\mathbf{r}) \tag{2.4}$$

E_n is the energy eigenvalue. Let us now introduce a translation operator T_λ such that

$$T_\lambda\Psi_n(\mathbf{r}) = \Psi_n(\mathbf{r}+\mathbf{R}_m) \tag{2.5}$$

where $\Psi(\mathbf{r})$ is the wave function. Now due to the symmetry of the crystal and the periodic nature of the potential we can assert that

$$\Psi_n(\mathbf{r}+\mathbf{R}_m) = t_\lambda\Psi_n(\mathbf{r}) \tag{2.6}$$

where t_λ is the phase factor and $|t_\lambda|^2 = 1$. Consequently the probability densities $|\Psi(\mathbf{r}+\mathbf{R}_m)|^2$ and $|\Psi(\mathbf{r})|^2$ at identical sites in the crystal will be the same as the symmetry and periodicity the crystal demands.

H and T_λ commute and thus have simultaneous eigenfunctions. This leads to Bloch's theorem which states that the wavefunction must satisfy the relationship

$$e^{i\mathbf{k}\cdot\mathbf{R}_m}\Psi_n(\mathbf{k},\mathbf{r}) = \Psi_n(\mathbf{k},\mathbf{r}+\mathbf{R}_m)\,. \tag{2.7}$$

This relationship is satisfied by a normalized Bloch wavefunction which has the form

$$\Psi_n(\mathbf{k},\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{L^{3/2}}u_n(\mathbf{k},\mathbf{r}) \tag{2.8}$$

where L^3 is the volume of the crystal. Here $u_n(\mathbf{k},\mathbf{r})$, the Bloch function, has the periodicity of the crystal lattice, that is

$$u_n(\mathbf{k},\mathbf{r}) = u_n(\mathbf{k},\mathbf{r}+\mathbf{R}_m) \tag{2.9}$$

Substituting the Bloch wavefunction into the Schrödinger equation 2.4 results in

$$\left(-\frac{\hbar^2}{2m_o}\left(\nabla + i\mathbf{k}\right)^2 + V_o\left(\mathbf{r}\right)\right) u_n\left(\mathbf{k},\mathbf{r}\right) = E_n\left(\mathbf{k}\right) u_n\left(\mathbf{k},\mathbf{r}\right) \tag{2.10}$$

with use of the relationship

$$\begin{aligned} \sum_j \frac{\partial^2}{\partial x_j^2}\Psi_n &= -k^2\Psi_n + 2i\sum k_j \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{L^{3/2}}\frac{\partial u_n}{\partial x_j} + \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{L^{3/2}}\sum_j \frac{\partial^2 u_n}{\partial x_j^2} \\ &= \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{L^{3/2}}\left(\nabla + i\mathbf{k}\right)^2 u_n \end{aligned} \tag{2.11}$$

Remembering that $\mathbf{p} \equiv i\hbar\nabla$ this can be rewritten in the form

$$\left(-\frac{\hbar^2}{2m_o}\nabla^2 + \frac{\hbar}{m_o}\mathbf{k}\cdot\mathbf{p} + V_o\left(\mathbf{r}\right)\right) u_n\left(\mathbf{k},\mathbf{r}\right) = \left(E_n\left(\mathbf{k}\right) - \frac{\hbar^2 k^2}{2m_o}\right) u_n\left(\mathbf{k},\mathbf{r}\right) \tag{2.12}$$

k·p Theory

There are different methods for deriving the energy bands of a semiconductor, such as the nearly free electron model and the linear combination of atomic orbitals, but the $\mathbf{k}\cdot\mathbf{p}$ method will be used here. This is a perturbation method where it is assumed that the band structure has been resolved at some point $\mathbf{k}_o$, a high symmetry point (usually the Γ point of the Brillouin zone), and that all the energy eigenvalues $E_n\left(\mathbf{k}_o\right)$ and corresponding Bloch functions $u_n\left(\mathbf{k}_o,\mathbf{r}\right)$ are known. The desired Bloch functions $u_n\left(\mathbf{k},\mathbf{r}\right)$ are then calculated by expanding in terms of the complete set of functions $u_{n'}\left(\mathbf{k}_o,\mathbf{r}\right)$. This also allows for the calculation of the corresponding eigenenergies $E_n\left(\mathbf{k}_o\right)$ which is achieved by rewriting

equation 2.12 as a perturbed Hamiltonian

$$\left(H_o + \frac{\hbar}{m_o}\mathbf{k}\cdot\mathbf{p}\right) u_n(\mathbf{k},\mathbf{r}) = \overline{E}_n(\mathbf{k})\, u_n(\mathbf{k},\mathbf{r}) \tag{2.13}$$

where

$$H_o = -\frac{\hbar^2}{2m_o}\nabla^2 + V_o(\mathbf{r}) \tag{2.14}$$

and

$$\overline{E}_n(\mathbf{k}) = E_n(\mathbf{k}) - \frac{\hbar^2 k^2}{2m_o} \tag{2.15}$$

For the nondegenerate case using second-order perturbation theory and with the assumption that $\mathbf{k}_o = 0$ we get

$$\overline{E}_n(\mathbf{k}) = E_n(0) + \sum_{l\neq n} \frac{\hbar^2}{m_o^2} \frac{\mathbf{k}\cdot\langle n|\,\mathbf{p}\,|l\rangle\,\mathbf{k}\cdot\langle l|\,\mathbf{p}\,|n\rangle}{E_n(0) - E_l(0)} \tag{2.16}$$

For a simple example assume two states $|0\rangle$ and $|1\rangle$ where the corresponding energies $E_0 = E_g$ and $E_1 = 0$ then the energy of the system is

$$\overline{E}_{0,1}(\mathbf{k}) = E_{0,1}(0) + \frac{\hbar^2 k^2}{2m_o} \pm \sum_{i,j} \frac{\hbar^2 k_i k_j}{m_o^2} \frac{2\wp_i^* \wp_j}{m_o E_g} \tag{2.17}$$

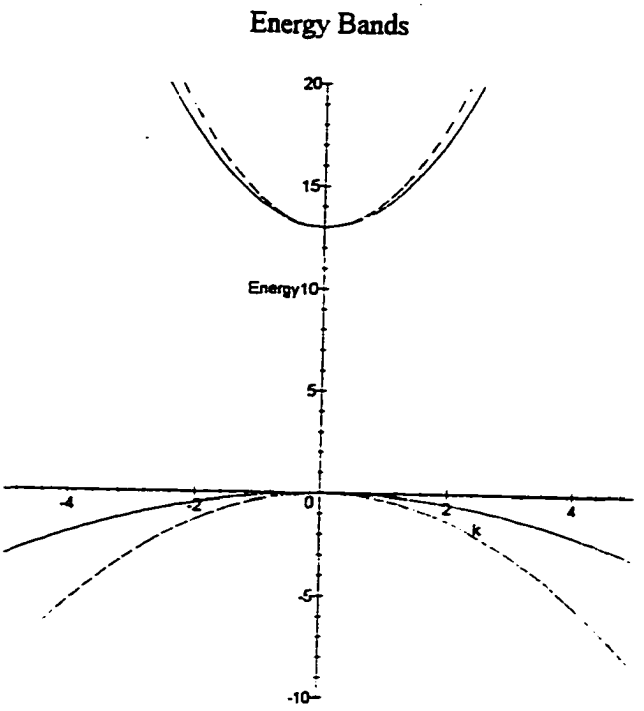
where $\wp_i = \langle 0|\,\mathbf{p}_i\,|1\rangle$ is a momentum matrix element. The positive solution of equation 2.17 is the solution for E_0 and the negative solution is for E_1, all other solutions will be zero due to orthogonality. These results are shown by the solid lines in Fig. 1. The form of the last two terms strongly suggests that an effective mass tensor

$$\frac{1}{m_{eff}} = \frac{1}{m_o}\left(\partial_{ij} \pm \frac{2\wp_i^* \wp_j}{m_o E_g}\right) \tag{2.18}$$

can be defined. This reduces to a scalar quantity for cubic symmetry, as in all isotropic cases, and can thus be expressed as

$$m_i = \frac{m_o}{1 + \sigma_i \frac{2p^2}{m_o E_g}} \text{ with } \sigma_c = 1 \text{ and } \sigma_v = -1 \tag{2.19}$$

If the momentum matrix element is sufficiently large the effective mass for the lower (valance, v) band is negative, while the effective mass of electrons in the conduction (c) band is much smaller than the free electron mass. This effective mass approximation is demonstrated by the dashed lines in Fig. 1.



This picture, while giving an intuitive feeling for the band structure of crystals, is not strictly correct as it ignores degeneracy of the valance band at the Γ point.

However the band structure model is clear enough to form a picture of the exciton in the semiconductor.

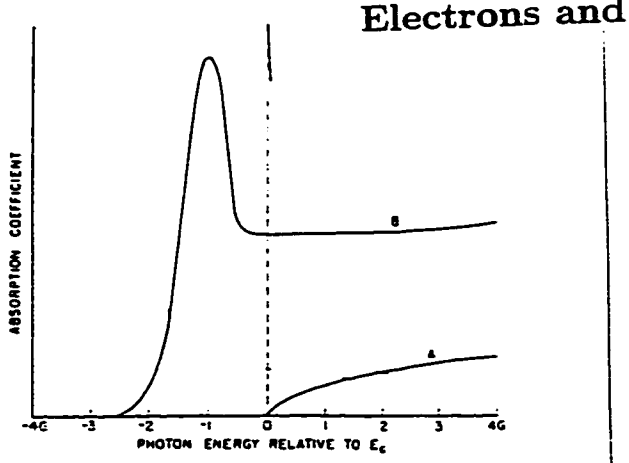


FIG. 24. Comparison of predictions of absorption edge shapes for the following modifications of simple band-to-band transitions. (A) No modification: Coulomb interaction and magnetic field absent. (B) Coulomb interaction only (normal exciton spectrum).

[13]

Fig. 2.

Electrons and Holes.

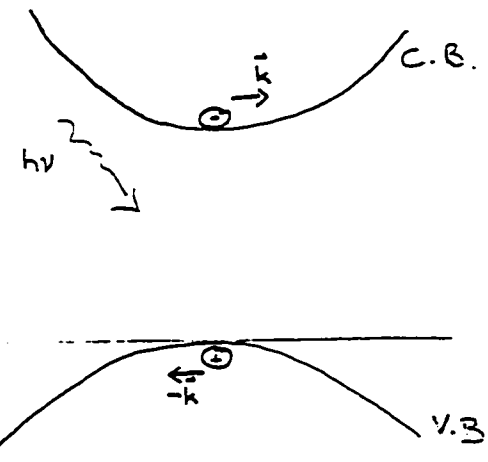


Fig. 3

The basic band structure of a semiconductor explains much of the optical properties of the semiconductor, absorption will occur when a valence band electron is excited with energy larger than the band gap. The excitation of an electron out of the valance band into the conduction band creates a vacant orbital in the valence band. This vacant orbital is called a hole and responds to an electric field as if it were a positively charged particle. The reasons for this are firstly that the total wavevector of the electrons in a filled band is zero. This is due to the geometrical symmetry of the Brillouin zone of a lattice, which has inversion symmetry. If the band is filled all its $\mathbf{k}$ states (both positive and negative) are filled, giving a total wavevector of zero. Thus if an electron with wavevector $\mathbf{k}_e$ is missing, then the valance band will have a wave vector $-\mathbf{k}_e$, which we attribute to the hole. The hole also has the opposite energy to the electron. This is once

again due to inversion symmetry. If the energy of the electron is $E_e(\mathbf{k}_e)$, then the energy of the hole is $E_h(\mathbf{k}_h) = -E_e(-\mathbf{k}_e)$. The properties of the hole are summarized in table 1 below.

Property	Hole	Removed electron	(2.20)
electric charge	$-q_e$	$q_e \approx -1.6 \times 10^{-19} C$	
wave vector	$-k_e$	k_e	
angular momentum	$-\sigma_e$	σ_e	
effective mass	$-m_h > 0$	$m_e < 0$	
particle statistic	fermion	fermion	

Table 1. Properties of Holes in Valence Band ([12])

There is an expectation that the absorption spectra of the semiconductor would begin at the band edge as seen in the solid line in figure 2. The semiconductor will begin to absorb as soon as we are able to excite an electron across the bandgap from the valance band to the conduction band (fig. 3). However the optical spectra of good quality semiconductors, at low temperature, are found to resemble the dotted line in figure 2 [13]. This is because the conduction band electron and the hole experience a Coulomb interaction allowing them to become bound together, thus allowing for absorption to occur at energies that are below the energy of the bandgap ($E_{bandgap} - E_{binding}$)(fig. 3). Semiconductors thus absorb at energies below the bandgap due to the binding energy of the pair or

exciton.

The exciton consists of a conduction band electron bound to a hole. Both the hole and the electron are fermions. If one thinks of the primary property of fermions being that they are antisymmetric under exchange of particles, then one would expect the exciton to be a boson. The exciton will be symmetric under exchange as this requires the interchange of both the electron and the hole. These two exchanges are antisymmetric giving two negatives, this results in a positive or symmetric exchange for the exciton, seeming to indicate that the exciton is a boson [14].

Chapter 3

Fermions and Bosons

In the previous chapter we described both electrons and holes as fermions and anticipated that the exciton might be a boson. Before we attempt to determine if the exciton is in fact a boson, a careful description of fermionic and bosonic properties is required.

Both fermions and bosons are indistinguishable particles but they obey different statistics. The primary difference between them being that fermions obey the Pauli exclusion principle, which states that there can never be more than one excitation in a particular state, whereas bosons are unrestricted in the number of particles that can exist in a state. A second principle difference is that fermions are antisymmetric while bosons are symmetric under exchange of particles. Antisymmetry dictates that the wave function of a system of fermions will obey the Pauli exclusion principle for the exchange of any two particles or excitations

$$\Psi\left(r_1,...,r_n,..r_m,...r_N\right) = -\Psi\left(r_1,...,r_m,..r_n,...r_N\right).$$

Here r_1, r_2... etc. refer to the position of the particles and their spin. However this thesis will not deal with spin. Bosons on the other hand are symmetric under

exchange of particles

$$\Psi(r_1, ..., r_n, ..r_m, ...r_N) = \Psi(r_1, ..., r_m, ..r_n, ...r_N).$$

A direct result of the symmetry of the two types of particle or excitation is that boson creation and annihilation operators obey commutation relations whereas fermion operators obey anticommutation relations.

In Fock space the wave function for a single particle fermion or boson system can be written as

$$\Psi_1(r_1) = \langle r_1 | 1_1, 0_2, 0_3, .. \rangle$$

here the first state is occupied by one fermion or boson while the rest of the states are empty. The annihilation and creation operators for both fermions and bosons change the occupation numbers of the states on which they act. The creation operator increases the occupation by one and the annihilation operator decreases the occupation number by one. The difference between excitons and fermions arising from the Pauli exclusion principle specifies that for fermions the occupation number can only be zero or one. For both fermions and bosons, for the unnormalized case,

$$a^\dagger |n\rangle = \sqrt{n+1}\, |n+1\rangle$$

$$a |n\rangle = \sqrt{n}\, |n-1\rangle$$

however for fermions the creation operator $\left(a^\dagger\right)$ can only act on a state where $n = 0$ and the fermion annihilation operator (a) can only act on a state $n = 1$. In

both the fermion and boson cases

$$a^{\dagger}|0\rangle = |1\rangle \text{ and } a|0\rangle = 0$$

but fermions must in addition also satisfy the condition that

$$a^{\dagger 2}|n\rangle = 0 \text{ and } a^2|n\rangle = 0.$$

We can create fermions and boson in different states

$$a_k^{\dagger} a_{k'}^{\dagger}|0\rangle = |1_k, 1_{k'}\rangle$$

which for fermions translates [15] into

$$\langle r_1, r_2| a_k^{\dagger} a_{k'}^{\dagger}|0\rangle = \frac{1}{\sqrt{2}}\left[\Psi_{k'}(r_1)\Psi_k(r_2) - \Psi_{k'}(r_2)\Psi_k(r1)\right].$$

The two fermions are indistinguishable and the Pauli exclusion principal demands that the exchange of particles be antisymmetric. Bosons, while also being indistinguishable, are symmetric under exchange such that

$$\langle r_1, r_2| a_k^{\dagger} a_{k'}^{\dagger}|0\rangle = \frac{1}{\sqrt{2}}\left[\Psi_{k'}(r_1)\Psi_k(r_2) + \Psi_{k'}(r_2)\Psi_k(r1)\right].$$

If the system were created in the opposite order, the bosons would remain unaffected

$$\begin{aligned}\langle r_1, r_2| a_{k'}^{\dagger} a_k^{\dagger}|0\rangle &= \frac{1}{\sqrt{2}}\left[\Psi_k(r_1)\Psi_{k'}(r_2) + \Psi_k(r_2)\Psi_{k'}(r1)\right] \\ &= \langle r_1, r_2| a_k^{\dagger} a_{k'}^{\dagger}|0\rangle\end{aligned}$$

but for the fermions

$$\begin{aligned}\langle r_1, r_2| a_{k'}^{\dagger} a_k^{\dagger}|0\rangle &= \frac{1}{\sqrt{2}}\left[\Psi_k(r_1)\Psi_{k'}(r_2) - \Psi_k(r_2)\Psi_{k'}(r1)\right] \\ &= \langle r_1, r_2| - a_k^{\dagger} a_{k'}^{\dagger}|0\rangle\end{aligned}$$

Thus we find that fermions satisfy

$$a^\dagger_{k'} a^\dagger_k + a^\dagger_k a^\dagger_{k'} |0\rangle = 0$$

so

$$a^\dagger_{k'} a^\dagger_k + a^\dagger_k a^\dagger_{k'} = 0.$$

This gives us one of the anticommutation relations

$$\left\{a^\dagger_k, a^\dagger_{k'}\right\} = a^\dagger_k a^\dagger_{k'} + a^\dagger_{k'} a^\dagger_k = 0.$$

Whereas for the bosons

$$a^\dagger_{k'} a^\dagger_k - a^\dagger_k a^\dagger_{k'} |0\rangle = 0$$

giving the commutation relation

$$\left[a^\dagger_k, a^\dagger_{k'}\right] = a^\dagger_k a^\dagger_{k'} - a^\dagger_{k'} a^\dagger_k = 0.$$

The hermitian conjugates are

$$\{a_k, a_{k'}\} = 0$$

for fermions and

$$[a_k, a_{k'}] = 0$$

for bosons. Thus these first two commutation relations are a direct result of the exchange symmetry of the particles.

Also for $k \neq k'$ in the fermionic case

$$\left\{a_k, a^\dagger_{k'}\right\} = 0$$

and in the bosonic case

$$\left[a_k, a_{k'}^\dagger\right] = 0.$$

To solve the $k = k'$ case we first need to consider the effect of acting on a state

$$\alpha |0_k\rangle + \beta |1_k\rangle$$

from which we can see that

$$\left(a_{k'} a_k^\dagger + a_k^\dagger a_{k'}\right)(\alpha |0_k\rangle + \beta |1_k\rangle) = \alpha |0_k\rangle + \beta |1_k\rangle$$

for fermions and consequently

$$\left\{a_k, a_k^\dagger\right\} = 1.$$

For bosons

$$\left(a_{k'} a_k^\dagger - a_k^\dagger a_{k'}\right)(\alpha |0_k\rangle + \beta |1_k\rangle) = \alpha |0_k\rangle + \beta |1_k\rangle$$

giving

$$\left[a_k, a_k^\dagger\right] = 1.$$

These results are summarized in the table below. These results show the intimate connection between the statistics of a particle or excitation and its commutation or anticommutation relations.

Anticommutation Relations	Commutation Relations
Fermions	Bosons
$\left\{a_k^\dagger, a_{k'}^\dagger\right\} = 0$	$\left[a_k^\dagger, a_{k'}^\dagger\right] = 0$
$\{a_k, a_{k'}\} = 0$	$[a_k, a_{k'}] = 0$
$\left\{a_k, a_{k'}^\dagger\right\} = \delta_{kk'}$	$\left[a_k, a_{k'}^\dagger\right] = \delta_{kk'}$
	condensation occurs

Table 2.

Now that the fermion and boson commutation relations have been looked at we can use them to derive the exciton commutation relations.

Chapter 4

Exciton Operators, A New Approach.

The previous chapter described the difference between fermion and boson commutation relations. This chapter will attempt to accurately describe the exciton commutation relations. This will occur by first describing an operator that describes the exciton as an electron and hole pair. The commutation relations for these pair operators will be derived. The pair operators will then be transformed into exciton operators thereby allowing for the derivation of the exciton commutation relations in terms of the exciton operators. Chapter 2 anticipated that the exciton commutation relations might be bosonic but this is found to only be approximately the case. The exciton commutation relations are usually expressed [7][8] as

$$[B_n, B_{n'}] = \left[B_n^\dagger, B_{n'}^\dagger\right] = 0$$

$$\left[B_n, B_{n'}^\dagger\right] = \delta_{n,n'} - O\left(\eta a_o^d\right)$$

where η is the exciton density present and a_o^d is the size of the exciton with d as the dimension of the system. These are approximately bosonic but with a correction

factor that is small provided the density of the excitons is small compared to the size of the exciton.

Here B_n and $B_n^\dagger$ are the operators that respectively annihilate and create an exciton in a Hydrogen-like state n. These operators are defined in terms of the unbound exciton operator $B_{\mathbf{k},\mathbf{K}}^\dagger$ (4.15) which is derived in this chapter. Given the symmetry displayed by the first two relations it is surprising that the third relationship reflects a partial exclusion principle. Consequently a closer look at exactly how the commutation relations vary from bosonic is warranted.

The electron and hole annihilation operators are defined as $\alpha_{\mathbf{k}} \equiv a_{c,\mathbf{k}}$ and $\beta_{-\mathbf{k}} \equiv a_{v,\mathbf{k}}^\dagger$ respectively. For an exciton to be formed an electron must be created in the conduction band, after destroying an electron in the valence band, thereby creating a hole in the valence band, with the opposite wavevector. In terms of the electron-hole operators the pair operator would then be $b_{\mathbf{k},-\mathbf{k}}^\dagger = \alpha_{\mathbf{k}}^\dagger \beta_{-\mathbf{k}}^\dagger$. This operator as it stands is not general for it assumes that the exciton was formed between the particular electron that was excited and the particular hole it left and also that they have zero centre of mass momentum. This is not the only possible pairing. Others pairs between exciting electrons in the conduction band and hole in the valance band will result in a centre on mass momentum. Consequently a more general expression of an pair operator is

$$b_{\mathbf{k},\mathbf{K}}^\dagger = \alpha_{\mathbf{k}+m_{re}\mathbf{K}}^\dagger \beta_{-\mathbf{k}+m_{rh}\mathbf{K}}^\dagger \tag{4.1}$$

where $\mathbf{K}$ is the center of mass (of the pair) wave vector, $\mathbf{k}$ is the relative wave

vector and

$$\mathbf{K}_i = \mathbf{k}_{ei} + \mathbf{k}_{hi}, \ \mathbf{k}_i = m_{rh}\mathbf{k}_{ei} - m_{re}\mathbf{k}_{hi}. \tag{4.2}$$

The electron, hole and total mass are m_e, m_h and M respectively and $m_{re} = \frac{m_e}{M}$ and $m_{rh} = \frac{m_h}{M}$. Where ever possible $k_i = \{k_i, K_i\}$ will be used to describe the i^{th} pair.

The fermion space in which the electron and holes exist does not allow for unique pairing. That is to say that a fermion space with two electrons e_1, e_2 and two holes h_1, h_2 does not correspond to a pair space with two pairs but rather to one with two possible pairings. That is the pairing can occur in two different ways $(e_1, h_1), (e_2, h_2)$ and $(e_1, h_2), (e_2, h_1)$. As such there is a one-to-$n!$ correspondence between fermion space and pair space. However each pairing is unique in that in each paired state the electron is only paired with one hole and as such has a unique centre of mass motion. Thus we can have a one-to-one correspondence between the fermion state and the pair state if the pair is restricted to maintain these unique centre of mass motions. All other pairing require that an exchange occurs.

Electrons are of course fermions and their operators consequently anticommute (chapter 3, table 2)

$$[\beta_{\mathbf{k}}, \beta_{\mathbf{k}'}]_+ = \left[\beta^\dagger_{\mathbf{k}}, \beta^\dagger_{\mathbf{k}'}\right]_+ = [\alpha_{\mathbf{k}}, \alpha_{\mathbf{k}'}]_+ = \left[\alpha^\dagger_{\mathbf{k}}, \alpha^\dagger_{\mathbf{k}'}\right]_+ = 0 \tag{4.3}$$

and

$$\left[\beta_{\mathbf{k}}, \beta^\dagger_{\mathbf{k}'}\right]_+ = \left[\alpha_{\mathbf{k}}, \alpha^\dagger_{\mathbf{k}'}\right]_+ = \delta_{\mathbf{k},\mathbf{k}'}. \tag{4.4}$$

It is shown in appendix A that

$$\left[a_n^\dagger a_m, a_r^\dagger a_s\right] = \delta_{m,r} a_n^\dagger a_s - \delta_{n,s} a_r^\dagger a_m. \tag{4.5}$$

Using relations 4.1 and 4.5 we find that the pair commutation relations

$$\left[b_{\mathbf{k}_i}, b_{\mathbf{k}_j}\right] = \left[b_{\mathbf{k}_i}^\dagger, b_{\mathbf{k}_j}^\dagger\right] = 0 \tag{4.6}$$

and

$$\left[b_{\mathbf{k}_i}, b_{\mathbf{k}_j}^\dagger\right] = \delta_{\mathbf{k}_i,\mathbf{k}_j} - \delta_{kh_i,kh_j}\alpha_{ke_j}^\dagger \alpha_{ke_i} - \delta_{ke_ike_j}\beta_{kh_jh_i}^\dagger \beta_{kh_i} \tag{4.7}$$

The fermion anticommutation relation $a_k a_{k'}^\dagger = \delta_{kk'} - a_{k'}^\dagger a_k$ does not allow the creation of a particle with quantum number k' if the already existing particle k has the same quantum numbers, $k' = k$. Similarly the exciton commutation relation will block the attempt to create the pair k_j if either the electron k_{e_j} or hole k_{h_j} exists previously. This reinforces the idea that the pairs are quasi-bosons and raises the question about their symmetry properties.

It would be beneficial to be able to express the pair commutation relation in terms of an exciton operator, this can be achieved using Usui's [4] transformation. Usui defines the operator

$$U = P_F \exp\left(\sum_{k_e k_h} B_{k_e k_h}^\dagger b_{k_e k_h}\right) P_B \tag{4.8}$$

where P_F and P_B are projection operators onto the fermion and pair vacuums, $|0\rangle_F$ and $|0\rangle_B$ respectively. This operator U acts in the fermion, quasi-bosonic product space and acts on a fermion state converting it into a quasi-bosonic state,

that is a linear combination of the possible pairs. He obtains

$$U\prod_{i=1}^{M}\alpha^{\dagger}_{ke_i}\beta^{\dagger}_{kh_i}\left|0\right\rangle=\sum_{P}(-1)^{P}P\prod_{i=1}^{M}B^{\dagger}_{ke_ikh_i}\left|0\right\rangle \tag{4.9}$$

where P is a permutation of k_{ei} and is due to the exchange of the holes, which due to their fermionic nature are antisymmetric. Thus the one-to-$n!$ correspondence between the two spaces is evident. However if an ordering operator O, is introduced, which results in a zero eigenvalue if the permutation P is not in compliance with the ordering prescription and is one otherwise, a one-to-one correspondence between the two spaces is ensured. Consequently

$$OU\prod_{i=1}^{M}\alpha^{\dagger}_{ke_i}\beta^{\dagger}_{kh_i}\left|0\right\rangle=\prod_{i=1}^{M}B^{\dagger}_{ke_ikh_i}\left|0\right\rangle .$$

The ordering operator is a projection operator and as such

$$O^2=O$$

The hermitian conjugate of U is

$$U^{\dagger}=P_B\exp\left(\sum_{k_ek_h}B_{k_ek_h}b^{\dagger}_{k_ek_h}\right)P_F \tag{4.10}$$

which transforms the boson state back to the corresponding fermion state

$$OU^{\dagger}\prod_{i=1}^{M}B^{\dagger}_{ke_ikh}\left|0\right\rangle=\prod_{i=1}^{M}\alpha^{\dagger}_{ke_i}\beta^{\dagger}_{kh_i}\left|0\right\rangle_i .$$

Thus $U^{\dagger}OU$ is necessarily unity and $OUA_FU^{\dagger}O$ transforms any fermion operator A_F to a boson operator A_B. Also the operator expectation value should remain unchanged

$${}_F\left\langle\Psi\right|A_F\left|\Phi\right\rangle_F={}_F\left\langle\Psi\right|U^{\dagger}O\left(OUA_FU^{\dagger}O\right)OU\left|\Phi\right\rangle_F$$

The transformation of zero being zero we initially find that

$$[B_{n_1}, B_{n_2}] = \left[B^\dagger_{n_1}, B^\dagger_{n_2}\right] = 0.$$

The transformation, as shown in appendix B, can be derived using the expansion

$$\exp\left(\sum_{k_e k_h} B_{k_e k_h} b^\dagger_{k_e k_h}\right) = \sum_{k=0}^{\infty} \frac{\left(\sum_{k_e k_h} B_{k_e k_h} b^\dagger_{k_e k_h}\right)^k}{k!}, \tag{4.11}$$

in combination with the fact that quasi-bosonic operators commutes with fermionic operators. The resulting transformation is

$$\alpha^\dagger_{ke_j} \alpha_{ke_i} = \sum_{kh} B^\dagger_{ke_i,kh} B_{ke_j,kh}$$

and

$$\beta^\dagger_{kh_j} \beta_{kh_i} = \sum_{ke} B^\dagger_{ke,kh_i} B_{ke,kh_j}. \tag{4.12}$$

This allows us to rewrite equation 4.7 as

$$\left[B_{\mathbf{k}_1}, B^\dagger_{\mathbf{k}2}\right] = \delta_{\mathbf{k}_1,\mathbf{k}_2} - \delta_{kh_1,kh_2} \sum_{kh} B^\dagger_{ke_i,kh} B_{ke_j,kh} - \delta_{ke_1 ke_2} \sum_{ke} B^\dagger_{ke,kh_i} B_{ke,kh_j}. \tag{4.13}$$

However there appears to be a problem with this result. In the situation where, for example, we have an existing pair $|k_e, k_{h1}; ...\rangle$ and where $k_e \neq k_{e1}$ and $k_{h1} \neq k_{h2}$ then the RHS of equation 4.13 becomes $-|k_e, k_{h2}; ...\rangle$. However, the LHS becomes $B_{\mathbf{k}_1} |k_e, k_{h1}; k_{e2}, k_{h2}; ...\rangle$ which will be zero, making the expression invalid unless $k_e = k_{e1}$. Consequently the summation will only select only the term with $k_e = k_{e1}$ (or k_{e2} as the delta function determines that the only non zero term will have $k_{e1} = k_{e2}$). Substituting k_{e1} (k_{h1}) and k_{e2} (k_{h2}) for k and k' the resulting

transformations can thus be expressed as

$$\alpha^{\dagger}_{ke_j}\alpha_{ke_i} = B^{\dagger}_{ke_i,kh_i}B_{ke_j,kh_j}$$

and

$$\beta^{\dagger}_{kh_j}\beta_{kh_i} = B^{\dagger}_{ke_i,kh_i}B_{ke_j,kh_j}.$$

Thus

$$\left[B_{\mathbf{k}_1}, B^{\dagger}_{\mathbf{k}2}\right] = \delta_{\mathbf{k}_1,\mathbf{k}_2} - 2\left(\delta_{kh_1,kh_2} + \delta_{ke_1,ke_2}\right)B^{\dagger}_{\mathbf{k}_2}B_{\mathbf{k}_1}. \tag{4.14}$$

A new exciton basis, which is a linear combination of the exciton operators, can be expressed as

$$B^{\dagger}_{n,\mathbf{K}} = \sum_{\mathbf{k}} \Psi_{n,\mathbf{k}} B^{\dagger}_{\mathbf{k},\mathbf{K}} \tag{4.15}$$

where $\Psi_{n,k}$ is the k-space representation of the new basis and in our case will be the hydrogen-like basis. The corresponding $d-$dimension wavefunction is

$$\Psi_n(\mathbf{r}) = \sum_{\mathbf{k}} \Psi_{n,\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{L^{\frac{d}{2}}} \tag{4.16}$$

where L is the length and $\mathbf{r}$ is a vector from the hole to the electron. This transformation does not change the center of mass motion of the pair. The inverse transformation is

$$B^{\dagger}_{\mathbf{k},\mathbf{K}} = \sum_{n} \Psi^{*}_{n,\mathbf{k}} B^{\dagger}_{n,\mathbf{K}}. \tag{4.17}$$

The commutation relation in this basis gives

$$\left[B_{n_1}, B^{\dagger}_{n_2}\right] = \sum_{\mathbf{k}_1\mathbf{k}_2} \Psi^{*}_{n_1\mathbf{k}_1}\Psi_{n_2\mathbf{k}_2}\left[B_{\mathbf{k}_1}, B^{\dagger}_{\mathbf{k}2}\right] \tag{4.18}$$

where $n_i = \{n_i, \mathbf{K}_i\}$ and using equation 4.14 and the inverse transformation 4.17 can be expressed as

$$\left[B_{n_1}, B^{\dagger}_{n_2}\right] = \delta_{n_1,n_2} - 2\sum_{m_2 m_1} \chi^{m_1,m_2}_{n_1,n_2} B^{\dagger}_{m_2} B_{m_1} \tag{4.19}$$

where $m_i = \{m_i, \mathbf{K}_i\}$ and

$$\chi^{m_1,m_2}_{n_1,n_2} = \sum_{\mathbf{k}} \Psi^{*}_{n_1,\mathbf{k}} \Psi_{n_2,\mathbf{k}} \Psi^{*}_{m_2,\mathbf{k}} \Psi_{m_1,\mathbf{k}}. \tag{4.20}$$

The resulting exciton operators are approximately bosonic. They are symmetric under exchange, however we see that there is also an exclusion principle at work. The derivation of the exciton commutation relations not only explicitly describes the deviation of these commutation relations from bosonic but also allows for the introduction of the physically more intuitive hydrogen-like exciton basis.

Chapter 5

Hydrogen-like Basis for the Exciton.

To better understand how the exciton commutation relations vary from bosonic behavior we need to look at the χ factor. This requires that a set of basis functions $\{\Psi_n\}$ be selected. The exciton strongly resembles a hydrogen atom, with a positive and a negative particle bound together by Coulombic forces, consequently a three dimensional hydrogen-like basis is chosen, giving a good match with the physics of the system. While this system can be worked out in one, two or three dimensions, the below example is worked out in three dimensions. The hydrogen like wavefunction is derived in the usual manner by separation of the function into the radial and spherical components [16], giving

$$\Psi_{nlm}(\mathbf{r},\theta,\phi) = R_{nl}(\mathbf{r})Y_{lm}(\theta,\phi)$$

and the eigenenergies of the system are

$$E_n = -\left(\frac{m^* e^4}{2\left(4\pi\epsilon\right)^2}\right)\frac{1}{\hbar^2 n^2}$$

and the Bohr radius is

$$a_o = \frac{4\pi\epsilon\hbar^2}{m^* e^2}.$$

Here n, l, and m are quantum numbers, ϵ is the effective dielectric constant, m^* is the effective mass and e is the elementary charge. The Fourier transform of the wavefunction is needed (equation 4.16) this transform was done using the spherical wave expansion of a plane wave,

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} i^l j_l(kr) \sum_{m=-l}^{l} Y_{lm}^*(\theta,\phi)\, Y_{lm}(\theta',\phi')$$

as described in Jackson [17]. This gives the general expression

$$\Psi_{nlm,\mathbf{k}} = \frac{4\pi}{\sqrt{V}} Y_{lm}(\theta',\phi')\, i^l \int_0^{\infty} r^2 j_l(kr)\, R_{nl}(r)\, dr.$$

Absorption of light is proportional to the square of the wave function evaluated at $\mathbf{r} = 0$ which is non-zero for s-states only [8]. Thus the s-hydrogen-like states will be calculated. The evaluation of the Fourier transform of the wavefunction using the spherical transformation, for s-states, gives

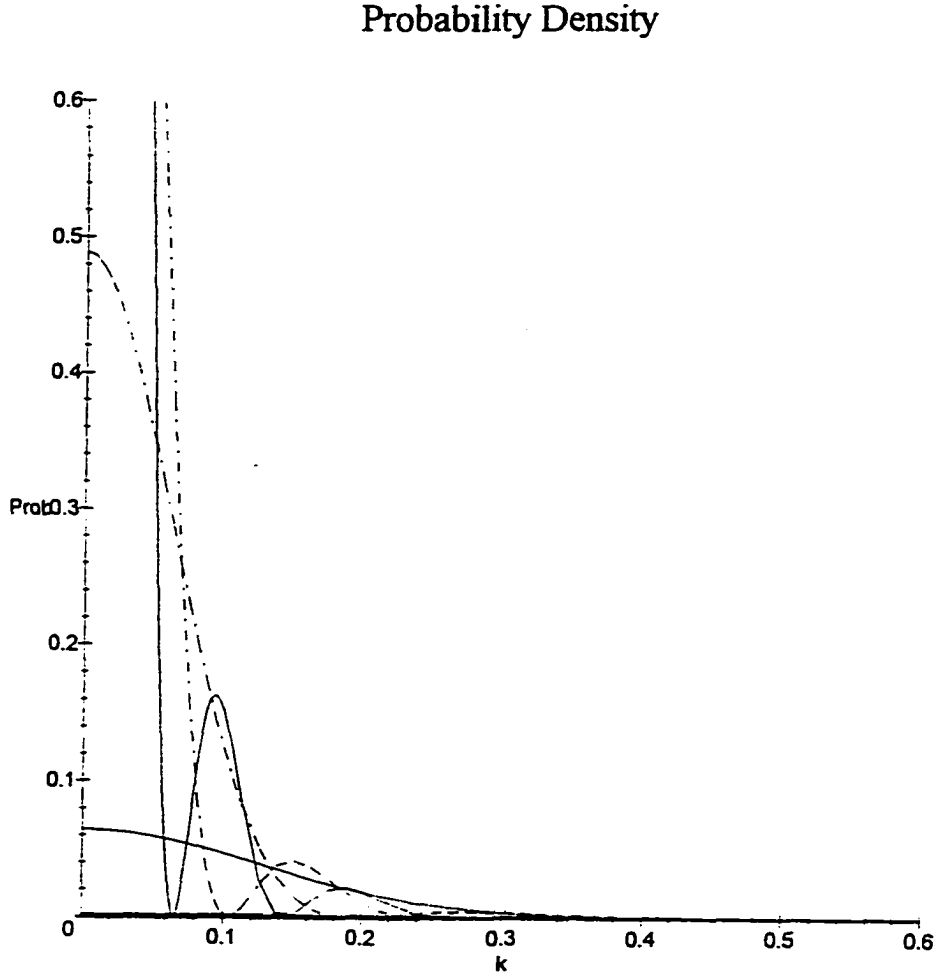
$$\Psi_{n00,\mathbf{k}} = 8n\sqrt{\pi}\left(\frac{na_o}{L}\right)^{\frac{3}{2}} \frac{P_n(nka_o)}{\left(1+(nka_o)^2\right)^{n+1}}$$

where $P_n(x)$ is a sequence of polynomials of order n

$$P_n(x) = \left\{1, x^2-1, 1-\frac{10}{3}x^2+x^4, 1-7x^2+7x^4-x^6, \ldots\right\}.$$

The Bohr radius a_o must be calculated using the effective mass and the effective dielectric constant of the crystal.

The probability distribution of these wavefunctions in k-space give an indication of the number of k-states available to each exciton.



The number of k-states that the 1s-exciton can occupy is seen to be much larger than the number of k-states that the 5-s exciton can occupy. Consequently we can create more 1s-excitons than a 5s-excitons. Also due to the phase space

filling properties of excitons the existence of any exciton will decrease the number of k-states available for the creation of any other exciton. The graph also indicates that existence of a 3s-exciton, for example, should have a more prohibitive effect on the creation of a 5s-exciton than the existence of a 1s-exciton or 2s-exciton would have.

The calculated χ parameters verify these trends. They are calculated by converting the sum in equation 4.20 to an integral, introducing a factor of $\left(\frac{L}{2\pi}\right)^3$. A factor of a_o^{-3} is also introduced when d^3k is converted to $d^3\left(a_o k\right)$ and as a result the χ parameter goes as $\left(\frac{a_o}{L}\right)^3$. This is the ratio of the size of the exciton to the size of the crystal. A new parameter η is defined, to extract this dependence, thus

$$\eta \equiv \left(\frac{L}{a_o}\right)^3 \chi.$$

The first few η parameters are given in Table 3. We have not shown the interference parameters (e.g. χ_{11}^{12}) but have rather concentrated on the effects between the excitons themselves, for example between the 1s-exciton and a 2s-exciton (χ_{22}^{11}) or with itself (χ_{11}^{11}).

$\eta_{11}^{11} = 51.84$	$\eta_{22}^{11} = 144.81$	$\eta_{33}^{11} = 165.13$	$\eta_{44}^{11} = 176.40$	$\eta_{55}^{11} = 183.13$
	$\eta_{22}^{22} = 1898$	$\eta_{33}^{22} = 3176$	$\eta_{44}^{22} = 3083$	$\eta_{55}^{22} = 4279$
		$\eta_{33}^{33} = 11832$	$\eta_{44}^{33} = 17070$	$\eta_{55}^{33} = 20400$
			$\eta_{44}^{44} = 40916$	$\eta_{55}^{44} = 54420$
				$\eta_{55}^{55} = 105050$

TABLE 3.

The η parameter goes approximately as n^5 which gives the order of magnitude trends in the table. The table also verifies the trends seen in the probability distribution graphs (Fig. 4). In fact the overlap of the exciton's k-space has the effect of reducing the probability of creating a new exciton (ν_1) by a factor of $1 - 2\left(\frac{a_o}{L}\right)^3 \sum_{\mu_1\mu_2} \eta_{\mu_1,\mu_2}^{\nu_1,\nu_1} B_\mu^\dagger B_\mu$ plus interference effects. Here $B_\mu^\dagger B_\mu$ counts the number of μ excitons. All existing excitons affect the creation of this new exciton, the extent of their contribution being indicated by the η factor. This contribution increases much faster than the size of the exciton (size of the exciton being $\propto (na_o)^3$) indicating that it is the state filling properties of the excitons not the size of the excitons which determine the number of excitons that can exist in a crystal.

The number of states available for the creation of 1s-excitons can be calculated

using the density of states, in k-space [18] and is

$$dN = \frac{V}{(2\pi)^3} d^3k.$$

Roughly speaking the k-space radius of a 1s-exciton is a_o^{-1}, consequently we can

$$\begin{aligned} N &\approx \frac{V}{(2\pi)^3} \frac{4}{3} \pi a_o^{-3} \\ &\approx \frac{V}{(6\pi^2)\, a_o^3}. \end{aligned}$$

Thus

$$\begin{aligned} \frac{1}{N} &\approx \frac{a_o^3}{V} \left(6\pi^2\right) \\ &\approx 59 \frac{a_o^3}{V}, \end{aligned}$$

this is approximately χ_{11}^{11} (which equals $\sim 52 \frac{a_o^3}{V}$) leading us to conclude that for the 1s-exciton

$$\frac{1}{N} \approx \chi.$$

Another way to think about χ is to look at is original definition, for example

$$\begin{aligned} \chi_{nn}^{nn} &= \sum_k |\Psi_{nk}|^4 \\ &= \sum_k \Psi_{nk}^* |\Psi_{nk}|^2 \Psi_{nk} \end{aligned}$$

this can be interpreted as the average of $|\Psi_{nk}|^2$, which is the probability distribution or occupancy probability, thus χ can be thought of as the average of the occupancy probability, or the average probability that the state is occupied.

The first part of this thesis has explicitly derived the commutation relations of the exciton, using the exciton operator. This relationship will be used in the second part of the thesis to determine the exciton dynamics.

Part II

Dynamics.

Chapter 6

Semiconductor Bloch Equations.

The second part of this thesis will use the Usui [4] transformation to write the interaction Hamiltonian in terms of the exciton operators. This will allow for the dynamics of the exciton to be calculated in the Heisenberg picture. These new dynamics will be compared with the semiconductor Bloch equations.

Excitons, the Coulomb Effect.

The semiconductor Bloch equations are traditionally used to describe exciton dynamics. To derive these equations we first need the Hamiltonian. In general the energy for an electron in a semiconductor can be expressed as

$$\widehat{H} = \sum_{\mathbf{k},i} E_{i,k} a^{\dagger}_{i,\mathbf{k}} a_{i,\mathbf{k}} = \sum_{\mathbf{k},i} E_{i,k} \hat{n}_{i,\mathbf{k}} \tag{6.1}$$

where $E_{i,k}$ is the energy of the particle and $\hat{n}_{i,\mathbf{k}} = a^{\dagger}_{i,\mathbf{k}} a_{i,\mathbf{k}}$ is the number operator. Here i is the band index and k is the crystal momentum.

The Coulomb potential must now be added to the Hamiltonian. The Coulomb potential can be written in general as an interaction $W(\mathbf{r} - \mathbf{r}')$ between two charge

densities $\rho_i(\mathbf{r})$

$$H_c = \frac{1}{2}\sum_{ij}\int W(\mathbf{r}-\mathbf{r}')\,\rho_i(\mathbf{r})\,\rho_j(\mathbf{r}')\,d^3r d^3r'.$$

Haug and Koch (pg. 115) [8] show that treating the ions as a uniform background charge distribution eliminates the $q = 0$ term. Transforming this result into Fourier space q, the Coulomb Hamiltonian becomes

$$H_c = \frac{1}{2}\sum_{\mathbf{q}\neq 0} W_q\left(\rho_{e,-\mathbf{q}}\rho_{e,\mathbf{q}} - e^2N\right) \tag{6.2}$$

where W_q is the Fourier transform of $W(\mathbf{r}-\mathbf{r}')$ and

$$\rho_{e,\mathbf{q}} = -e^2\sum_{j=1}^{N} e^{-i\mathbf{q}\cdot\mathbf{r}_j}.$$

To get the second quantized form necessary for the operator method we introduce the charge density operator $\hat{\rho}_{e,\mathbf{q}}$ and the number operator $\widehat{N}$ to replace the charge density and N the total number of electrons. The charge density operator is

$$\hat{\rho}_e(\mathbf{r}) = -e\hat{n}(\mathbf{r}) = -e\sum\hat{\Psi}^{\dagger}(\mathbf{r})\,\hat{\Psi}(\mathbf{r}) \tag{6.3}$$

where the field operators [8], are

$$\hat{\Psi}(\mathbf{r}) = \sum_{\mathbf{k},i} a_{i,\mathbf{k}}\Psi_i(k,\mathbf{r}) \tag{6.4}$$

where $\Psi_i(k,\mathbf{r})$ are the Bloch functions. Inserting equation 6.4 into equation 6.3 and taking the Fourier transform results in

$$\hat{\rho}_{e,\mathbf{q}} = -e\sum_{i,\mathbf{k}} a^{\dagger}_{i,\mathbf{k}-\mathbf{q}}a_{i,\mathbf{k}}.$$

which when substituted into equation 6.2, in its second quantized form gives

$$H_c = \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}\neq 0} V_q a^\dagger_{\mathbf{k}+\mathbf{q}} a_{\mathbf{k}} a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}'} - \frac{1}{2} \sum_{\mathbf{q}\neq 0} \widehat{N} V_{\mathbf{q}} \tag{6.5}$$

with $V_{\mathbf{q}} = e^2 W_{\mathbf{q}}$. Rearranging the operators using the anti-commutation relations and adding in the single particle energy (equation 6.1) we can get the Hamiltonian for an electron in a semiconductor taking into account the Coulomb potential of the other electrons in the material, giving

$$H_e = \sum_{\mathbf{k},i} E_{i,k} a^\dagger_{i,\mathbf{k}} a_{i,\mathbf{k}} + \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}\neq 0,i,j} V_q a^\dagger_{\mathbf{i},\mathbf{k}+\mathbf{q}} a^\dagger_{j,\mathbf{k}'-\mathbf{q}} a_{j,\mathbf{k}'} a_{i,\mathbf{k}}. \tag{6.6}$$

It is shown in Klingshirn (pg. 50-54) [12] that the $\widehat{\mathbf{p}}\cdot\widehat{\mathbf{A}}$ in the minimal coupling Hamiltonian can be replaced $e\mathbf{r}\cdot\mathcal{E}(\mathbf{r},t)$ assuming that the energy difference between the final an the initial state of the electron is equal to the photon frequency multiplied by $\hbar$. This then resembles a dipole in an electric field. This allows us to write the interaction Hamiltonian, for the semiconductor in an external field, in second quantized form as

$$H_I = \int \hat{\Psi}^\dagger(\mathbf{r}) [e\mathbf{r}] \cdot \mathcal{E}(\mathbf{r},t) \hat{\Psi}(\mathbf{r}) \, d^3r.$$

Assuming that the space and time parts of the electromagnetic field are separable

$$E(\mathbf{r},t) = \mathcal{E}(t) \frac{1}{2} \left[e^{i\mathbf{q}\cdot\mathbf{r}} + e^{-i\mathbf{q}\cdot\mathbf{r}} \right]$$

then using the expansion 6.4, the dipole approximation ($\lim_{q\to 0}$) and the two-band approximation ($\{i \neq j\} = \{c, v\}$), where c, v are the conduction and valence band

respectively, we get

$$H_I \simeq -\sum_{\mathbf{k}} E(t)\left(a^{\dagger}_{c,\mathbf{k}}a_{v,\mathbf{k}}d_{cv} + a_{c\mathbf{k}}a^{\dagger}_{v\mathbf{k}}d^{*}_{cv}\right). \tag{6.7}$$

Here d_{cv} is defined as the projection of the dipole $\mathbf{d}_{cv}$ in the direction of the field $\frac{\mathbf{E}}{E}$ or $\langle\Psi_c|\, e\mathbf{r}\,|\Psi_v\rangle$. Thus the total Hamiltonian for the two-band approximation is

$$\begin{aligned} H_e &= \sum_{\mathbf{k}}\left[E_{c,k}\hat{a}^{\dagger}_{c,\mathbf{k}}\hat{a}_{c,\mathbf{k}} + E_{v,k}\hat{a}^{\dagger}_{v,\mathbf{k}}\hat{a}_{v,\mathbf{k}}\right] \\ &+\frac{1}{2}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}\neq 0} V_q\left[a^{\dagger}_{c,\mathbf{k}+\mathbf{q}}a^{\dagger}_{c,\mathbf{k}'-\mathbf{q}}a_{c,\mathbf{k}'}a_{c,\mathbf{k}} + a^{\dagger}_{v,\mathbf{k}+\mathbf{q}}a^{\dagger}_{v,\mathbf{k}'-\mathbf{q}}a_{v,\mathbf{k}'}a_{v,\mathbf{k}} + 2a^{\dagger}_{c,\mathbf{k}+\mathbf{q}}a^{\dagger}_{v,\mathbf{k}'-\mathbf{q}}a_{v,\mathbf{k}'}a_{c,\mathbf{k}}\right] \\ &-\sum_{\mathbf{k}}\mathcal{E}(t)\left(a^{\dagger}_{c,\mathbf{k}}a_{v,\mathbf{k}}d_{cv} + a_{c\mathbf{k}}a^{\dagger}_{v\mathbf{k}}d^{*}_{cv}\right). \end{aligned} \tag{6.8}$$

In the effective mass approximation

$$E_{c,k} = \hbar\epsilon_{c,k} = E_g + \frac{\hbar^2k^2}{2m_e} \tag{6.9}$$

and

$$E_{v,k} = \hbar\epsilon_{v,k} = \frac{\hbar^2k^2}{2m_h} \tag{6.10}$$

m_e and m_h are the electron and hole effective mass respectively.

Exciton Dynamics - The Semiconductor Bloch Equations.

To derive the semiconductor Bloch equations the Hamiltonian is converted to one in the basis of electron and hole operators, where the electron operator is

$$\alpha^{\dagger}_{\mathbf{k}} \equiv a^{\dagger}_{c,\mathbf{k}} \tag{6.11}$$

and the hole operator is

$$\beta^{\dagger}_{-\mathbf{k}} \equiv a_{v,\mathbf{k}}. \tag{6.12}$$

The expectation values of the counting operators for electrons and holes can be expressed as

$$\left\langle \alpha_{\mathbf{k}}^{\dagger}\alpha_{\mathbf{k}} \right\rangle = n_{e,\mathbf{k}}(t), \tag{6.13}$$

$$\left\langle \beta_{-\mathbf{k}}^{\dagger}\beta_{-\mathbf{k}} \right\rangle = n_{h,\mathbf{k}}(t) \tag{6.14}$$

where the expectation value is defined as

$$\langle A \rangle = \int \Psi^{*}(k)\, A\Psi(k)\, dk.$$

The k^{th} component of the interband polarization is defined as

$$\langle \beta_{-\mathbf{k}}\alpha_{\mathbf{k}} \rangle = P_{eh}(\mathbf{k},t) \equiv P_{\mathbf{k}}(t). \tag{6.15}$$

Using this representation the Hamiltonian, equation 6.8, becomes

$$\begin{aligned} H_e \;=\; & \sum_{\mathbf{k}} \left[E_{e,k}\alpha_{c,\mathbf{k}}^{\dagger}\alpha_{c,\mathbf{k}} + E_{h,k}\beta_{v,-\mathbf{k}}^{\dagger}\beta_{v,-\mathbf{k}} \right] \\ & + \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}\neq 0} V_q \left[\alpha_{c,\mathbf{k}+\mathbf{q}}^{\dagger}\alpha_{c,\mathbf{k}'-\mathbf{q}}^{\dagger}\alpha_{c,\mathbf{k}'}\alpha_{c,\mathbf{k}} + \beta_{v,\mathbf{k}+\mathbf{q}}^{\dagger}\beta_{v,\mathbf{k}'-\mathbf{q}}^{\dagger}\beta_{v,\mathbf{k}'}\beta_{v,\mathbf{k}} \right. \\ & \qquad \left. + 2\alpha_{c,\mathbf{k}+\mathbf{q}}^{\dagger}\beta_{v,\mathbf{k}'-\mathbf{q}}^{\dagger}\beta_{v,\mathbf{k}'}\alpha_{c,\mathbf{k}} \right] \\ & - \sum_{\mathbf{k}} \mathcal{E}(t) \left(\alpha_{c,\mathbf{k}}^{\dagger}\beta_{v,-\mathbf{k}}^{\dagger} d_{cv} + \alpha_{c\mathbf{k}}\beta_{v,-\mathbf{k}} d_{cv}^{*} \right) \end{aligned} \tag{6.16}$$

where we define the energies as

$$E_{e,k} = E_{c,k} = \hbar\epsilon_{e,k}$$

and Coulomb exchange energy is included in the energy term for the hole as

$$E_{h,k} = -E_{v,k} + \sum_{q\neq 0} V_q = \hbar\epsilon_{h,k}.$$

Thus the interband transition energy is

$$\triangle E_k = E_{c,k} - E_{v,k} + \sum_{q \neq 0} V_q.$$

The calculation of the equations of motion using equations 6.13,6.14 and 6.15 give

$$\begin{aligned} \hbar \left[i\frac{d}{dt} - (\epsilon_{c,k} - \epsilon_{h,k}) \right] P_{\mathbf{k}}(t) &= [n_{e,\mathbf{k}}(t) + n_{h,\mathbf{k}}(t) - 1]\, d_{cv}\mathcal{E}(t) \\ &+ \sum_{\mathbf{k}',\mathbf{q}\neq 0} V_q[\left\langle \alpha^{\dagger}_{\mathbf{k}'+\mathbf{q}}\beta_{\mathbf{k}-\mathbf{q}}\alpha_{\mathbf{k}'}\alpha_{\mathbf{k}} \right\rangle + \left\langle \beta_{\mathbf{k}'+\mathbf{q}}\beta_{\mathbf{k}-\mathbf{q}}\beta^{\dagger}_{\mathbf{k}'}\alpha_{\mathbf{k}} \right\rangle \\ &+ \left\langle \alpha^{\dagger}_{\mathbf{k}'+\mathbf{q}}\beta_{\mathbf{k}-\mathbf{q}}\alpha_{\mathbf{k}'}\alpha_{\mathbf{k}} \right\rangle + \left\langle \beta_{\mathbf{k}'+\mathbf{q}}\beta_{\mathbf{k}-\mathbf{q}}\beta^{\dagger}_{\mathbf{k}'}\alpha_{\mathbf{k}} \right\rangle] \end{aligned} \quad (6.17)$$

for polarization, and

$$\begin{aligned} \hbar\frac{\partial}{\partial t} n_{e,\mathbf{k}}(t) &= -2\ \mathrm{Im}\ [d_{cv}\mathcal{E}(t)\, P^{*}_{\mathbf{k}}] \\ &+ i \sum_{\mathbf{k}',\mathbf{q}\neq 0} V_q[\left\langle \alpha^{\dagger}_{\mathbf{k}}\alpha^{\dagger}_{\mathbf{k}'-\mathbf{q}}\alpha_{\mathbf{k}-\mathbf{q}}\alpha_{\mathbf{k}'} \right\rangle - \left\langle \alpha^{\dagger}_{\mathbf{k}+\mathbf{q}}\alpha^{\dagger}_{\mathbf{k}'-\mathbf{q}}\alpha_{\mathbf{k}}\alpha_{\mathbf{k}'} \right\rangle \\ &+ \left\langle \alpha^{\dagger}_{\mathbf{k}}\alpha_{\mathbf{k}-\mathbf{q}}\beta^{\dagger}_{\mathbf{k}'-\mathbf{q}}\beta_{\mathbf{k}'} \right\rangle - \left\langle \alpha^{\dagger}_{\mathbf{k}+\mathbf{q}}\alpha_{\mathbf{k}}\beta^{\dagger}_{\mathbf{k}'-\mathbf{q}}\beta_{\mathbf{k}'} \right\rangle] \end{aligned} \quad (6.18)$$

$$\begin{aligned} \hbar\frac{\partial}{\partial t} n_{h,\mathbf{k}}(t) &= -2\ \mathrm{Im}\ [d_{cv}\mathcal{E}(t)\, P^{*}_{\mathbf{k}}] \\ &+ i \sum_{\mathbf{k}',\mathbf{q}\neq 0} V_q[\left\langle \beta^{\dagger}_{-\mathbf{k}}\beta^{\dagger}_{\mathbf{k}'-\mathbf{q}}\beta_{-\mathbf{k}-\mathbf{q}}\beta_{\mathbf{k}'} \right\rangle - \left\langle \beta^{\dagger}_{-\mathbf{k}+\mathbf{q}}\beta^{\dagger}_{\mathbf{k}'-\mathbf{q}}\beta_{-\mathbf{k}}\beta_{\mathbf{k}'} \right\rangle \\ &+ \left\langle \alpha^{\dagger}_{\mathbf{k}'+\mathbf{q}}\alpha_{\mathbf{k}'}\beta^{\dagger}_{-\mathbf{k}}\beta_{-\mathbf{k}+\mathbf{q}} \right\rangle - \left\langle \alpha^{\dagger}_{\mathbf{k}'+\mathbf{q}}\alpha_{\mathbf{k}'}\beta^{\dagger}_{-\mathbf{k}-\mathbf{q}}\beta_{-\mathbf{k}} \right\rangle] \end{aligned} \quad (6.19)$$

for the electron and hole counting operators respectively.

In the semiconductor Bloch equations the random phase approximation is used to reduce the four operator expectation values into the product of two relevant two operator expectation values, usually the density and interband polarization. It is assumed that these two terms dominate the properties of the system. The

justification being that the polarization expectation value $P_{vc} = \left\langle a^{\dagger}_{v,\mathbf{k}} a_{c,\mathbf{k}'} \right\rangle$ has a dominant time dependence when $\mathbf{k} = \mathbf{k}'$ as

$$\left\langle a^{\dagger}_{v,\mathbf{k}} a_{c,\mathbf{k}'} \right\rangle \propto e^{i(\omega_{\mathbf{k}} - \omega_{\mathbf{k}'})t}$$

which will oscillate rapidly thereby averaging to zero when $\mathbf{k} \neq \mathbf{k}'$. Thus

$$\left\langle a^{\dagger}_{c,\mathbf{k}'+\mathbf{q}} a^{\dagger}_{v,\mathbf{k}-\mathbf{q}} a_{c,\mathbf{k}'} a_{c,\mathbf{k}} \right\rangle \simeq P_{vc,\mathbf{k}'} n_{c,\mathbf{k}} \delta_{\mathbf{k}-\mathbf{q},\mathbf{k}'}.$$

However to keep the expression more general the correction terms to the random phase approximation can, at least formally, be kept. Using techniques as described by Haug and Koch [8] the semiconductor Bloch equations can be expressed as follows

$$\frac{\partial}{\partial t} P_{\mathbf{k}}(t) = -i\left(e_{e,k} + e_{h,k}\right) P_{\mathbf{k}} - i\ \left[n_{e,\mathbf{k}}(t) + n_{h,\mathbf{k}}(t) - 1\right] \omega_{R,\mathbf{k}} + \frac{\partial}{\partial t} P_{\mathbf{k}}|_{col} \quad (6.20)$$

$$\frac{\partial}{\partial t} n_{e,\mathbf{k}}(t) = -2\ \mathrm{Im}\ \left[\omega_{R,\mathbf{k}} P^{*}_{\mathbf{k}}\right] + \frac{\partial}{\partial t} n_{e,\mathbf{k}}|_{col} \quad (6.21)$$

$$\frac{\partial}{\partial t} n_{h,\mathbf{k}}(t) = -2\ \mathrm{Im}\ \left[\omega_{R,\mathbf{k}} P^{*}_{\mathbf{k}}\right] + \frac{\partial}{\partial t} n_{h,\mathbf{k}}|_{col} \quad (6.22)$$

where we have introduced the renormalized frequencies

$$e_{i,k} = \epsilon_{i,k} + \Xi_{exc,i}(k) \quad (6.23)$$

with the exchange self-energy being

$$\hbar \Xi_{exc,i}(k) = -\sum_{\mathbf{q} \neq \mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} n_{i,\mathbf{q}} \quad (6.24)$$

as derived in Koch and Haug (pg. 161-163)[8]. The last terms are the collision terms which are the result of a correction term to the derivation of the semiconductor Bloch equations. We have also defined the generalized Rabi frequency as

$$\omega_{R,\mathbf{k}} = \frac{1}{\hbar}\left[d_{cv}E(t) + \sum_{\mathbf{q}\neq\mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|}P_{\mathbf{q}}\right] \tag{6.25}$$

indicating that the system does not respond to the applied field but rather to the effective field which is the sum of the applied field and the Coulomb interactions due to the pairs. All the momentum states of the semiconductor Bloch equations while not appearing coupled in the equation are in fact coupled through the generalized Rabi frequency (6.25) and through the exchange energy (6.23 and 6.24). The -2 Im $[\omega_{R,\mathbf{k}}P^*_{\mathbf{k}}]$ terms in equations 6.21 and 6.22 describe the generation of electron and hole pairs by the absorption of light. The rate of change of the electron population is the same as the rate of change of the hole population if scattering, due to the correction terms, is ignored.

Chapter 7

The Exciton Hamiltonian and its Dynamics.

The Hamiltonian.

In the previous chapter the Hamiltonian for the exciton and the exciton dynamics were derived using electron and hole operators. In this picture the semiconductor Bloch equations are used and the excitons are still treated as pairs; electrons and holes that experience a Coulomb attraction. These operators are fermionic. In this chapter the Hamiltonian is rewritten by transforming these fermionic operators into quasi-bosonic exciton operators which allows for the description of the Hamiltonian and the dynamics of excitons while treating them as hydrogen-like particles rather than pairs.

The Hamilton in terms of the electron and hole operators,

$$\begin{aligned} H_e &= \sum_{\mathbf{k}} \left[E_{e,k} \alpha^{\dagger}_{c,\mathbf{k}} \alpha_{c,\mathbf{k}} + E_{h,k} \beta^{\dagger}_{v,-\mathbf{k}} \beta_{v,-\mathbf{k}} \right] \\ &\quad + \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}\neq 0} V_q \left[\alpha^{\dagger}_{c,\mathbf{k}+\mathbf{q}} \alpha^{\dagger}_{c,\mathbf{k}'-\mathbf{q}} \alpha_{c,\mathbf{k}'} \alpha_{c,\mathbf{k}} + \beta^{\dagger}_{v,\mathbf{k}+\mathbf{q}} \beta^{\dagger}_{v,\mathbf{k}'-\mathbf{q}} \beta_{v,\mathbf{k}'} \beta_{v,\mathbf{k}} - 2\alpha^{\dagger}_{c,\mathbf{k}+\mathbf{q}} \beta^{\dagger}_{v,\mathbf{k}'-\mathbf{q}} \beta_{v,\mathbf{k}'} \alpha_{c,\mathbf{k}} \right] \\ &\quad - \sum_{\mathbf{k}} \mathcal{E}(t) \left(\alpha^{\dagger}_{c,\mathbf{k}} \beta^{\dagger}_{v,-\mathbf{k}} d_{cv} + \alpha_{c\mathbf{k}} \beta_{v,-\mathbf{k}} d^{*}_{cv} \right), \end{aligned} \tag{7.1}$$

is transformed using Usui's transformation as described in chapter 4. The details of the transformation are given in appendix C. The transformation results in the first two terms when combined giving

$$H_o = \sum_{k_1} E^o_{k1} B^\dagger_{k1} B_{k1}$$

where $E^o_{k1} = E_{e,k} + E_{h,k}$ and $ki = \{k_{ei}, k_{hi}\}$. The electric field interaction term is transformed to

$$H_I = -\sum_{k1} \mathcal{E}(t) \left(B^\dagger_{k1} d_{cv} + B_{k1} d^*_{cv} \right).$$

The first of the potential terms, the hole-hole interaction, is transformed giving

$$H_{v1} = \frac{1}{2} \sum_{\substack{k1,k2 \\ q \neq 0}} V_q \left[B^\dagger_{k_{h1}, k_{e1}+q} B^\dagger_{k_{h2}, k_{e2}-q} B_{k2} B_{k1} - B^\dagger_{k_{h1}, k_{e2}-q} B^\dagger_{k_{h2}, k_{e1}+q} B_{k2} B_{k1} \right].$$

The second potential term, the electron-electron interaction, gives

$$H_{v2} = \frac{1}{2} \sum_{\substack{k1,k2, \\ q \neq 0}} V_q \left[B^\dagger_{k_{h1}+q, k_{e1}} B^\dagger_{k_{h2}-q, k_{e2}} B_{k2} B_{k1} - B^\dagger_{k_{h2}-q, k_{e1}} B^\dagger_{k_{h1}+q, k_{e2}} B_{k2} B_{k1} \right].$$

While the third potential term, the electron-hole interaction, gives four terms

$$\begin{aligned} H_{v3} = & \sum_{\substack{k1,k2 \\ q \neq 0}} V_q [B^\dagger_{k_{h1}-q, k_{e1}+q} B_{k_{h1}, k_{e1}} - B^\dagger_{k_{h2}-q, k_{e1}+q} B^\dagger_{k_{h1}, k_{e2}} B_{k2} B_{k1} - B^\dagger_{k_{h2}, k_{e1}+q} B^\dagger_{k_{h1}-q, k_{e2}} B_{k2} B_{k1} \\ & + B^\dagger_{k_{h1}, k_{e1}+q} B^\dagger_{k_{h2}-q, k_{e2}} B_{k2} B_{k1}]. \end{aligned}$$

This transformed Hamiltonian matches the Hamiltonian derived in Hanamura and Haug [7], except for the electromagnetic field term which was not included in their derivation. Rewriting this expression in terms of the direct terms and exchange terms gives

$$H = H_o + H_I + H_D + H_E.$$

Here

$$H_o = \sum_{k_1} E^o_{k1} B^\dagger_{k1} B_{k1} + \sum_{k1,q\neq 0} V_q B^\dagger_{k_{h1}-q,k_{e1}+q} B_{k_{h1},k_{e1}}.$$

describes the independent motion of the excitons and the Coulomb attraction between the electron and the hole of the exciton and the H_I term remains the unchanged. The Coulomb attraction between excitons comes from the third term. The direct Coulomb interaction terms refer to the terms where the exciton electron or hole either gains or losses momentum but the electron and hole remain paired

$$H_D = \frac{1}{2} \sum_{\substack{k1,k2 \\ q\neq 0}} V_q \left[B^\dagger_{k_{h1},k_{e1}+q} B^\dagger_{k_{h2},k_{e2}-q} + 2B^\dagger_{k_{h1},k_{e1}+q} B^\dagger_{k_{h2}-q,k_{e2}} + B^\dagger_{k_{h1}+q,k_{e1}} B^\dagger_{k_{h2}-q,k_{e2}} \right] B_{k2} B_{k1}.$$

The Coulomb exchange terms refer to the terms in which the electrons or holes are exchanged between two excitons as well as possible gaining or losing of momentum

$$\begin{aligned} H_E \;=\; & -\frac{1}{2} \sum_{\substack{k1,k2 \\ q\neq 0}} V_q [B^\dagger_{k_{h1},k_{e2}-q} B^\dagger_{k_{h2},k_{e1}+q} + B^\dagger_{k_{h2}-q,k_{e1}} B^\dagger_{k_{h1}+q,k_{e2}} + 2B^\dagger_{k_{h2}-q,k_{e1}+q} B^\dagger_{k_{h1},k_{e2}} \\ & + 2B^\dagger_{k_{h2},k_{e1}+q} B^\dagger_{k_{h1}-q,k_{e2}}] B_{k2} B_{k1}. \end{aligned}$$

The Hamiltonian is now rewritten in terms of the relative and center of mass wave vectors (see Appendix D). The direct center of mass and relative wave vectors remain as defined by equation 4.2 in Chapter 4. However after exchange the relative and center of mass wave vectors become

$$\mathbf{k}_{E1} = \mathbf{k}_1 + m_{rh}\mathbf{k}_{12}, \mathbf{K}_{E1} = \mathbf{K}_1 + \mathbf{k}_{21}, \mathbf{k}_{E2} = \mathbf{k}_2 - m_{rh}\mathbf{k}_{21}, \mathbf{K}_{E2} = \mathbf{K}_2 - \mathbf{k}_{21}$$

where

$$\mathbf{k}_{21} \equiv m_{re}(\mathbf{K}_2 - \mathbf{K}_1) + \mathbf{k}_2 + \mathbf{k}_1.$$

The Hamiltonian then becomes

$$H_o = \sum_{\mathbf{k}_1} E^o_{\mathbf{k}1} B^\dagger_{\mathbf{k}1} B_{\mathbf{k}1} + \sum_{\mathbf{q}\neq 0} V_q B^\dagger_{\mathbf{k}_1+q,\mathbf{K}_1} B_{\mathbf{k}_1}$$

$$H_I = -\sum_{\mathbf{k}1} \mathcal{E}(t) \left(d_{cv} B_{\mathbf{k}1,\mathbf{K}_1} + h.c\right)$$

$$\begin{aligned} H_D &= \sum_{\mathbf{k}_1\mathbf{k}_2} V_q [B^\dagger_{\mathbf{k}_1-m_{re}q,\mathbf{K}_1+q} B^\dagger_{\mathbf{k}_2+m_{re}q,\mathbf{K}_1-q} + 2B^\dagger_{\mathbf{k}_1+m_{rh}q,\mathbf{K}_1+q} B^\dagger_{\mathbf{k}_2+m_{re}q,\mathbf{K}_2-q} \\ &\quad + B^\dagger_{\mathbf{k}_1+m_{rh}q,\mathbf{K}_1+q} B^\dagger_{\mathbf{k}_2-m_{rh}q,\mathbf{K}_2-q}] B_{k2} B_{k1} \end{aligned}$$

$$\begin{aligned} H_E &= -\frac{1}{2} \sum_{\substack{\mathbf{k}_1,\mathbf{k}_2 \\ \mathbf{q}\neq 0}} V_q [B^\dagger_{\mathbf{k}_{E2}-m_{rh}q,\mathbf{K}_{E2}-q} B^\dagger_{\mathbf{k}_{E1}+m_{rh}q,\mathbf{K}_{E1}+q} + B^\dagger_{\mathbf{k}_{E2}+m_{re}q,\mathbf{K}_{E2}-q} B^\dagger_{\mathbf{k}_{E1}-m_{re}q,\mathbf{K}_{E1}+q} \\ &\quad + 2B^\dagger_{\mathbf{k}_{E2}+q,\mathbf{K}_{E2}} B^\dagger_{\mathbf{k}_{E1}} + 2B^\dagger_{\mathbf{k}_{E2}+m_{re}q,\mathbf{K}_{E2}-q} B^\dagger_{\mathbf{k}_{E1}+m_{rh}q,\mathbf{K}_{E1}+q}] B_{k2} B_{k1}. \end{aligned} \tag{7.2}$$

Referring back to equations 6.9 and 6.10 the single pair energy is $E^o_{\mathbf{k}1} = \frac{\hbar^2 k^2}{2\mu} + \frac{\hbar^2 K^2}{2M}$ and the Fourier transform of the Coulomb potential is $V_q = \left(\frac{2\pi}{L}\right)^d \frac{e^2}{\epsilon q^2}$. Here μ is effective mass, ϵ is the dielectric constant, d is the dimension and L is the length of the system. The Hamiltonian is now transformed into an exciton basis using equation 4.15. This transformation is worked out in appendix E, giving

$$H_o = \sum_{v_1} E^o_{v1} B^\dagger_{v1} B_{v1}$$

$$H_I = -\sum_{v1} \mathcal{E}(t) \left(d_{cv} \Psi_{n1}(\mathbf{r}=0) L^{-\frac{d}{2}} B_{n1,\mathbf{K}_1} + h.c\right)$$

$$H_c = \frac{1}{2} \sum_{\substack{v1,v2 \\ \mathbf{q}\neq 0}} \left[W^{n1,n2,q}_{n3,n4} B^\dagger_{n1,\mathbf{K}_1+q} B^\dagger_{n2,\mathbf{K}_2-q} - W^{n1,n2,q}_{n3,n4} B^\dagger_{n1,\mathbf{K}_{E1}-q} B^\dagger_{n2,\mathbf{K}_{E2}+q}\right] B_{v2} B_{v1} \tag{7.3}$$

where H_c is the combined direct and exchange Coulomb interactions, $v_i = \{n_i, \mathbf{K}_i\}$ and

$$W^{n1,n2,q}_{n3,n4} = \sum_{\substack{\mathbf{k}_1,\mathbf{k}_2 \\ q\neq 0}} V_q[F^{n1,n2,q}_{n3,n4}(\mathbf{k}_1 + m_{rh}q, \mathbf{k}_2 - m_{rh}q) + F^{n1,n2,q}_{n3,n4}(\mathbf{k}_1 - m_{re}q, \mathbf{k}_2 + m_{re}q) + F^{n1,n2,q}_{n3,n4}(\mathbf{k}_1 + m_{rh}q, \mathbf{k}_2 + m_{re}q)] \tag{7.4}$$

is the exciton pair potential, with

$$F^{n1,n2,q}_{n3,n4}(\mathbf{a}, \mathbf{b}) \equiv \Psi^*_{n1}(\mathbf{a})\,\Psi^*_{n2}(\mathbf{b})\,\Psi_{n3}(\mathbf{k}_2)\,\Psi_{n4}(\mathbf{k}_1).$$

The exciton energy now includes the band gap energy, E_g, the energy of the new basis, E_n, and the center of mass energy

$$E^o_v = E_g + E_n + \frac{\hbar^2 K^2}{2M}.$$

This Hamiltonian is once again quite similar to the total Hamiltonian in boson space as derived by Hanamura and Haug [7], without the external field, and is the same as that derived by Hawton and Nelson [19], which includes the external field.

Exciton Dynamics.

The Hamiltonian now allows for the calculation of the exciton dynamics using the Heisenberg equation

$$i\hbar\frac{dA}{dt} = [A, H].$$

For excitons operators that satisfy the commutation relations in chapter 4, equation 4.18 the above Hamiltonian, as derived in [19], gives

$$-i\hbar\frac{d}{dt}B_v^\dagger = E_v^o B_v^\dagger - \sum_{v1}\left(\mathcal{E}(t)\,d_{cv}\Psi_{n1}(0)\,L^{-\frac{d}{2}} + h.c.\right)\left(\delta_{v1,v} - 2\sum_{m1,m}\chi_{m1,m}^{n1,n,\mathbf{K}_1-\mathbf{K}}B_\mu^\dagger B_{\mu 1}\right) + \sum_{v1,n3,n4,\mathbf{Q}}\widetilde{W}_{n3,n4,\mathbf{Q}}^{n1,n,\mathbf{K}_1-\mathbf{K}_2}B_{n4,\mathbf{K}_1+\mathbf{Q}}^\dagger B_{n3,\mathbf{K}_2-\mathbf{Q}}^\dagger B_{v1} + X_v. \tag{7.5}$$

The effective exciton-exciton Coulomb interaction term is simply the exciton pair potential with a phase space filling correction to the exciton energy which is defined as

$$\widetilde{W}_{n3,n4,\mathbf{Q}}^{n1,n,\mathbf{K}_1-\mathbf{K}_2} \equiv W_{n3,n4,\mathbf{Q}}^{n1,n,\mathbf{K}_1-\mathbf{K}_2} + 2\delta_{\mathbf{Q},0}E_{v1}^o\chi_{n3,n1}^{n4,n,\mathbf{K}_1-\mathbf{K}_2}.$$

There is also a small phase space filling correction term that affects the Coulomb term, which is defined as

$$X_v \equiv \sum_{\substack{v1,n3,n4,\mathbf{Q},\\ v2,m1,m}} W_{n3,n4,\mathbf{Q}}^{n1,n2,\mathbf{K}_1-\mathbf{K}_2}\chi_{m2,m}^{n2,n,\mathbf{K}_2-\mathbf{K}}B_{n4,\mathbf{K}_1+\mathbf{Q}}^\dagger B_{n3,\mathbf{K}_2-\mathbf{Q}}^\dagger\left(B_{v1}B_{\mu 2}^\dagger B_\mu + B_{\mu 2}^\dagger B_\mu B_{v1}\right).$$

So the first line of equation 7.5 includes the zero order terms and an external driving term that has been corrected for phase space filling. The second line includes all exciton-exciton interactions. These phase space filling effects, χ, are not included in the Hanamura and Haug [7] dynamics and are of a similar magnitude to the Coulomb term X_v.

To make the boson approximation, so often used for excitons, χ is set to zero. The origin of the phase space filling properties of the exciton are a result of the fermionic properties of the free electrons and hole. This can be understood in terms of an simple analogy used in Jacobson *et al* [1], which points out that

individual two state atoms, like the free electrons and holes, are fermionic in that they can only accept a single quanta of energy. That is to say the Pauli exclusion principle is at work. However a large ensemble of these atoms can be viewed as bosonic in the sense that the system, at low excitations, will easily accept another quanta of energy. This is true until it begins to reach the 50 % excited level at which time the excitation is as likely to de-excite one of the fermions as it is to excite another fermion.

As defined in the previous chapter, equation 6.15, the k^{th} component of the polarization is $P_{\mathbf{k}}(t) = \langle \beta_{-\mathbf{k}} \alpha_{\mathbf{k}} \rangle$,which is identified with $\langle B_{\mathbf{k}} \rangle$, thus the polarization semiconductor Bloch equation can be derived by taking the expectation value of equation 7.5. While Hawton and Nelson [19] show that decay due to dephasing should be taken into account for comparisons with experiment we will use their result but will ignore dephasing. Given this Hawton and Nelson show that the expectation value is

$$\begin{aligned} -i\hbar\frac{d}{dt}\left\langle B_v^\dagger \right\rangle &= E_v^o \left\langle B_v^\dagger \right\rangle \\ &\quad - \sum_{v1} \left(\mathcal{E}(t)\, d_{cv} \Psi_{n1}(0)\, L^{-\frac{d}{2}} + h.c. \right) \left(\delta_{v1,v} - 2 \sum_{m1,m} \chi_{m1,m}^{n1,n,\mathbf{K}_1-\mathbf{K}} \left\langle B_\mu^\dagger B_{\mu 1} \right\rangle \right) \\ &\quad + \sum_{v1,n3,n4,\mathbf{Q}} \widetilde{W}_{n3,n4,\mathbf{Q}}^{n1,n,\mathbf{K}_1-\mathbf{K}_2} \left\langle B_{n4,\mathbf{K}_1+\mathbf{Q}}^\dagger B_{n3,\mathbf{K}_2-\mathbf{Q}}^\dagger B_{v1} \right\rangle + O\left(\mathcal{R}^5\right). \end{aligned} \tag{7.6}$$

where $\mathcal{R} \equiv \mathcal{E}(t)\, d_{cv} \Psi_{n1}(0) \frac{L^{-\frac{d}{2}}}{\hbar}$. This can be re-expressed in the free pair basis as

$$\begin{aligned} \left(i\hbar\frac{d}{dt} + E_{v1}^o \right) \left\langle B_{\mathbf{k}}^\dagger \right\rangle &= \mathcal{E}(t)\, d_{cv} \left(1 - 2\left\langle B_{\mathbf{k}_1}^\dagger B_{\mathbf{k}_1} \right\rangle \right) \\ &\quad + \sum_{\mathbf{q}\neq\mathbf{0}} V_{\mathbf{q}} \left(\left\langle B_{\mathbf{k}_1}^\dagger \right\rangle - 2\left\langle B_{\mathbf{k}+\mathbf{q}}^\dagger B_{\mathbf{k}}^\dagger B_{\mathbf{k}} \right\rangle + 2\left\langle B_{\mathbf{k}}^\dagger B_{\mathbf{k}+\mathbf{q}}^\dagger B_{\mathbf{k}+\mathbf{q}} \right\rangle \right) + O\left(\mathcal{R}^5\right). \end{aligned} \tag{7.7}$$

If $\left\langle B^{\dagger}_{\mathbf{k+q}} B^{\dagger}_{\mathbf{k}} B_{\mathbf{k}} \right\rangle$ and $\left\langle B^{\dagger}_{\mathbf{k}} B^{\dagger}_{\mathbf{k+q}} B_{\mathbf{k+q}} \right\rangle$ are factorized to the fourth order in the field, which is possible if damping is ignored [19], into the polarization and number operator parts giving $\left\langle B^{\dagger}_{\mathbf{k+q}} \right\rangle \left\langle B^{\dagger}_{\mathbf{k}} B_{\mathbf{k}} \right\rangle$ and $\left\langle B^{\dagger}_{\mathbf{k}} \right\rangle \left\langle B^{\dagger}_{\mathbf{k+q}} B_{\mathbf{k+q}} \right\rangle$ respectively then for zero center of mass momentum, equation 7.8 compares favorably to the polarization semiconductor Bloch equation 6.20, derived in the previous chapter. Here the collision term is the Coulomb interaction term in equation 7.5 which is incorporated into the $O\left(\mathcal{R}^5\right)$ term, and which would involve a change in the center of mass momentum.

Consequently we see that the semiconductor Bloch equations can be derived from the new commutation relations using exciton operators in the hydrogen-like basis. This derivation is advantageous as it clearly distinguishes the assumptions necessary to attain the above equation and also allows for the dynamics of non-zero center of mass momentum excitons to be explored.

As shown in [19] the linear approximation to equation 7.8 is identical to the equation of motion derived in Axt *et al* [11]. In these papers Axt *et al* cite many experiments where the semiconductor Bloch equations are too limited to explain the experimental results. The Axt *et al* equations of motions, like the above derived equations of motion, allow for higher order field effects, resulting in better agreement with experiment.

Chapter 8

Conclusion.

This thesis began with the use of electron and hole operators to describe the excitation of a semiconductor, these operators are fermionic. Pair operators were then defined using these hole and electron operators. These pair operators were found to be quasi-bosonic. A transformation was used to convert these pair operators to exciton operators. The commutation relations of these exciton operators were also found to obey statistics intermediate between fermions and bosons. The exciton operators were then transformed to a hydrogen-like basis that incorporated the intra-pair Coloumb interactions. The manner in which the exciton operators statistics vary from bosonic to fermionic was discussed in more detail.

The Hamiltonian for an excited semiconductor in an external electromagnetic field was derived and transformed so that it was expressed in terms of the exciton operators and reflected the quasi-boson statistics of the exciton operators. The dynamics of the system was calculated in the Heisenberg picture. The Hawton and Nelson derivation in [19] of the expectation values of these dynamic equations agreed with the semiconductor Bloch equations, provided the new equations were terminated at the fourth order. This derivation clearly showed that the semi-

conductor Bloch equations primarily deal with excitons with zero center of mass momentum, where the collision terms deal with the interactions which change the center of mass momentum.

Future Studies.

The nature of the exciton statistics might with further study might lead to greater understanding of the exciton, it has been speculated that it might give an insight into the phase space size of the exciton and also throw some more light on the condensation of excitons discussions. The exciton operator approach allows for the introduction of the exciton hydrogen-like basis which gives a better connection between the theory and the physics of the system.

This approach will make it easier to calculate nonlinear optical effects such as the optical Stark effect, pump-probe effects and higher order responses to an external field. These findings also allow for the explanation of, and possible prediction of higher intensity optical phenomena, such as those discussed in Jacobson *et al* [1]. High intensity lasers are now more readily available and consequently the old assumption of excitons as bosons becomes very restrictive for experimental explanations, thus demanding that the statistics of excitons be further explored.

Appendices

A. Appendix A.

Commutation Relations of Four Fermion Operators.

We know that fermions obey the anti commutation relations specified in chapter 3, table 2. So if $a_i^\dagger$ and a_i are the fermion creation and annihilation operators respectively then

$$\begin{aligned}
\left[a_r^\dagger a_s, a_k^\dagger a_m\right] &= a_r^\dagger a_s a_k^\dagger a_m - a_k^\dagger a_m a_r^\dagger a_s \\
&= a_r^\dagger a_s a_k^\dagger a_m - a_k^\dagger \left(\delta_{mr} - a_r^\dagger a_m\right) a_s \\
&= a_r^\dagger a_s a_k^\dagger a_m - a_k^\dagger \delta_{mr} a_s + a_k^\dagger a_r^\dagger a_m a_s \\
&= a_r^\dagger a_s a_k^\dagger a_m - a_k^\dagger \delta_{mr} a_s + \left(0 - a_r^\dagger a_k^\dagger\right) a_m a_s \\
&= a_r^\dagger a_s a_k^\dagger a_m - a_k^\dagger \delta_{mr} a_s - a_r^\dagger a_k^\dagger a_m a_s \\
&= a_r^\dagger a_s a_k^\dagger a_m - a_k^\dagger \delta_{mr} a_s - a_r^\dagger a_k^\dagger \left(0 - a_s a_m\right) \\
&= a_r^\dagger a_s a_k^\dagger a_m - a_k^\dagger \delta_{mr} a_s + a_r^\dagger a_k^\dagger a_s a_m \\
&= a_r^\dagger \left(\delta_{sk} - a_k^\dagger a_s\right) a_m - a_k^\dagger \delta_{mr} a_s + a_r^\dagger a_k^\dagger a_s a_m
\end{aligned}$$

$$= a_r^\dagger \delta_{sk} a_m - a_r^\dagger a_k^\dagger a_s a_m - a_k^\dagger \delta_{mr} a_s + a_r^\dagger a_k^\dagger a_s a_m$$

$$= a_r^\dagger \delta_{sk} a_m - a_k^\dagger \delta_{mr} a_s.$$

To summarize

$$\left[a_r^\dagger a_s, a_k^\dagger a_m\right] = a_r^\dagger \delta_{sk} a_m - a_k^\dagger \delta_{mr} a_s.$$

B. Appendix B.

Usui's Transformation for the Commutation Relations.

The fermion operator $\alpha_k^\dagger \alpha_{k'}$ can be transformed into a boson operator using the Usui transformation (equation 4.8). In the below expression r_i and R_i are the electron and hole subscripts respectively.

$$OU_N \alpha_k^\dagger \alpha_{k'} U_{N'}^\dagger = \frac{1}{(N!)^2} O \sum_{\substack{r_i=1 \text{ to } N \\ R_i=1 \text{ to } N}} \left[\left(B_{r_1 R_1}^\dagger \beta_{r_1} \alpha_{R_1} B_{r_2 R_2}^\dagger \beta_{r_2} \alpha_{R_2} \ldots B_{r_N R_N}^\dagger \beta_{r_N} \alpha_{R_N}\right)\left(\alpha_k^\dagger \alpha_{k'}\right)\right.$$
$$\left.\left(B_{r'_N R'_N} \alpha_{R'_N}^\dagger \beta_{r'_N}^\dagger \ldots B_{r'_2 R'_2} \alpha_{R'_2}^\dagger \beta_{r'_2}^\dagger B_{r'_1 R'_1} \alpha_{R'_1}^\dagger \beta_{r'_1}^\dagger\right)\right] \tag{B.1}$$

The boson operators commute with the fermion operators, and electrons and hole operators will be antisymmetric under exchange. Consequently, the RHS of equation B.1 can be rewritten as

$$= \frac{O}{(N!)^2} \sum_{\substack{r_i=1 \text{ to } N \\ R_i=1 \text{ to } N}} (-1)^{P_{r_i}} (-1)^{P_{R_i kk'}} \left[\left(B_{r_1 R_1}^\dagger B_{r_2 R_2}^\dagger \ldots B_{r_N R_N}^\dagger B_{r'_N R'_N} \ldots B_{r'_2 R'_2} B_{r'_1 R'_1}\right)\left(\beta_{r_1} \beta_{r_2} \ldots \beta_{r_N}\right)\right.$$
$$\left.\left(\beta_{r'_N}^\dagger \ldots \beta_{r'_2}^\dagger \beta_{r'_1}^\dagger\right)\left(\alpha_{R_1} \alpha_{R_2} \ldots \alpha_{R_N} \alpha_k^\dagger \alpha_{k'} \alpha_{R'_N}^\dagger \ldots \alpha_{R'_2}^\dagger \alpha_{R'_1}^\dagger\right)\right].$$

Evaluation of the electron and hole operators, using the fermion commutation relations, acting on the fermion vacuum results in the various permutations of the

new boson operators, which can be expressed as

$$= \frac{1}{(N!)^2} O \sum_{\substack{r_i=1 \text{ to } N \\ R_i=1 \text{ to } (N-1)}} (-1)^{P_{r_i}} (-1)^{P_{R_i kk'}} P_{r_i} P_{R_i kk'} \left[\left(B^{\dagger}_{r_1 R_1} B^{\dagger}_{r_2 R_2} ... B^{\dagger}_{r_N k} B_{r_N k'} ... B_{r_2 R_2} B_{r_1 R_1} \right) \right].$$

There are $N!$ equivalent permutations of the pairs leaving only permutations of the electrons. Equating these gives

$$= \frac{1}{N!} O \sum_{\substack{r_i=1 \text{ to } N \\ R_i=1 \text{ to } (N-1)}} (-1)^{P_{R_i kk'}} P_{R_i kk'} \left[\left(B^{\dagger}_{r_1 R_1} B^{\dagger}_{r_2 R_2} ... B^{\dagger}_{r_N k} B_{r_N k'} ... B_{r_2 R_2} B_{r_1 R_1} \right) \right].$$

The ordering operator ensures that only the pair or pairs involved in the exchange can be altered, the remaining dummy variables (r_i, R_i) must remain unchanged. The Boson operators commute with themselves allowing us to write

$$= \frac{1}{N!} \sum_{\substack{r_i=1 \text{ to } N \\ R_i=1 \text{ to } (N-1)}} (-1)^{P_{kk'}} P_{kk'} \left[\left(B^{\dagger}_{r_N k} ... B^{\dagger}_{r_2 R_2} B^{\dagger}_{r_1 R_1} B_{r_1 R_1} B_{r_2 R_2} ... B_{r_N k'} \right) \right].$$

There are N possible permutations of the $B_{r_N k'}$'s and the remaining arrangements of boson operators will simply count the number of excitons not involved in the interaction, $(N-1)$ excitons in this case, leaving us with

$$\alpha^{\dagger}_k \alpha_{k'} = \sum_{r_i} \left(B^{\dagger}_{r_N k} B_{r_N k'} \right).$$

Similarly we find that

$$\beta^{\dagger}_k \beta_{k'} = \sum_{R_i} \left(B^{\dagger}_{k R_N} B_{k' R_N} \right).$$

C. Appendix C.

Usui Transformation of the Hamiltonian.

The electron-electron interaction $\alpha^{\dagger}_{k2-q}\alpha^{\dagger}_{k1+q}\alpha_{k1}\alpha_{k2}$ is transformed using the Usui transformation (equation 4.8) allowing us to write it in terms of the exciton operators. Here r_i and R_i are the electron and hole subscripts respectively and the exciton operators are always written in the form $B_{ke,kh}$.

$$\begin{aligned} OU_N\alpha^{\dagger}_{k2-q}\alpha^{\dagger}_{k1+q}\alpha_{k1}\alpha_{k2}U^{\dagger}_{N'} &= \frac{1}{(N!)^2}O\sum_{\substack{r_i=1\text{ to }N\\ R_i=1\text{ to }N}}[\left(B^{\dagger}_{r_1R_1}\beta_{r_1}\alpha_{R_1}B^{\dagger}_{r_2R_2}\beta_{r_2}\alpha_{R_2}...B^{\dagger}_{r_NR_N}\beta_{r_N}\alpha_{R_N}\right) \\ &\quad \left(\alpha^{\dagger}_{k2-q}\alpha^{\dagger}_{k1+q}\alpha_{k1}\alpha_{k2}\right) \\ &\quad \left(B_{r'_NR'_N}\alpha^{\dagger}_{R'_N}\beta^{\dagger}_{r'_N}...B_{r'_2R'_2}\alpha^{\dagger}_{R'_2}\beta^{\dagger}_{r'2}B_{r'_1R'_1}\alpha^{\dagger}_{R'_1}\beta^{\dagger}_{r'_1}\right)] \end{aligned} \tag{C.2}$$

In a identical manner to the transformations derived in appendix A, using the ordering operator we find that

$$OU_N\alpha^{\dagger}_{k2-q}\alpha^{\dagger}_{k1+q}\alpha_{k1}\alpha_{k2}U^{\dagger}_{N'} = \sum_{r1,r2}\left[B^{\dagger}_{r1,k1+q}B^{\dagger}_{r2,k2-q}B_{r2,k2}B_{r1,k1} - B^{\dagger}_{r1,k2-q}B^{\dagger}_{r2,k1+q}B_{r2,k2}B_{r1,k1}\right].$$

Similarly for the hole-hole interaction

$$OU_N\beta^{\dagger}_{k2-q}\beta^{\dagger}_{k1+q}\beta_{k1}\beta_{k2}U^{\dagger}_{N'} = \sum_{R1,R2}\left[B^{\dagger}_{k1+q,R1}B^{\dagger}_{k2-q,R2}B_{k2,R2}B_{k1,R1} - B^{\dagger}_{k2-q,R1}B^{\dagger}_{k1+q,R2}B_{k2,R2}B_{k1,R1}\right].$$

The transformation of electron-hole interaction by a similar process produces four terms rather than two, giving

$$\begin{aligned} OU_N\alpha^{\dagger}_{k2-q}\beta^{\dagger}_{k1+q}\beta_{k1}\alpha_{k2}U^{\dagger}_{N'} &= \sum_{r1,R1}[B^{\dagger}_{r1,R1}B^{\dagger}_{k1+q,k2-q}B_{k1,k2}B_{r1,R1} - B^{\dagger}_{r1,R1}B^{\dagger}_{k1+q,k2-q}B_{k1,R1}B_{r1,k2} \\ &\quad -B^{\dagger}_{r1,k2-q}B^{\dagger}_{k1+q,R1}B_{k1,k2}B_{r1,R1} + B^{\dagger}_{r1,k2-q}B^{\dagger}_{k1+q,R1}B_{k1,R1}B_{r1,k2}]. \end{aligned}$$

D. Appendix D.

Center of Mass and Relative Wave Vectors.

The center of mass and relative wave vector are specified as

$$\mathbf{K}_i = k_{ei} + k_{hi} \tag{D.3}$$

and

$$\mathbf{k}_i = m_{rh} k_{ei} - m_{re} k_{hi} \tag{D.4}$$

respectively.

Direct Coulomb Terms.

To rewrite the direct term $B^{\dagger}_{kh1,ke1+q} B^{\dagger}_{kh2,ke2-q} B_{kh2,ke2} B_{kh1,ke1}$ in terms of the center of mass and relative wave vector we need to recognize that

$$k_{e1} \rightarrow k_{e1} + q \text{ and } k_{e2} \rightarrow k_{e2} - q$$

while

$$k_{h1} \rightarrow k_{h1} \text{ and } k_{h2} \rightarrow k_{h2}.$$

Thus

$$\begin{aligned} \mathbf{K}_1 &= k_{e1} + q + k_{h1} \\ &= \mathbf{K}_1 + q \\ \mathbf{K}_2 &= k_{e2} - q + k_{h2} \\ &= \mathbf{K}_2 - q \end{aligned}$$

and

$$\begin{aligned}\mathbf{k}_1 &= m_{rh}\left(k_{e1}+q\right)-m_{re}k_{h1}\\ &= \mathbf{k}_1+m_{rh}q\end{aligned}$$

$$\begin{aligned}\mathbf{k}_2 &= m_{rh}\left(k_{e2}-q\right)-m_{re}k_{h2}\\ &= \mathbf{k}_2-m_{rh}q.\end{aligned}$$

The term then becomes

$$B^{\dagger}_{\mathbf{k}_1+m_{rh}q,\mathbf{K}_1+q}B^{\dagger}_{\mathbf{k}_2-m_{rh}q,\mathbf{K}_2-q}B_{\mathbf{k}_2}B_{\mathbf{k}_1}.$$

The same process allows us to find the other terms

$$B^{\dagger}_{kh1+q,ke1}B^{\dagger}_{kh2-q,ke2}B_{kh2,ke2}B_{kh1,ke1}=B^{\dagger}_{\mathbf{k}_1-m_{re}q,\mathbf{K}_1+q}B^{\dagger}_{\mathbf{k}_2+m_{re}q,\mathbf{K}_2-q}B_{\mathbf{k}_2}B_{\mathbf{k}_1}$$

and

$$B^{\dagger}_{kh1,ke1+q}B^{\dagger}_{kh2-q,ke2}B_{kh2,ke2}B_{kh1,ke1}=B^{\dagger}_{\mathbf{k}_1+m_{rh}q,\mathbf{K}_1+q}B^{\dagger}_{\mathbf{k}_2+m_{re}q,\mathbf{K}_2-q}B_{\mathbf{k}_2}B_{\mathbf{k}_1}. \quad \text{(D.5)}$$

The Exchange Terms.

The exchange terms can be rewritten using the relationships

$$k_{ei}=m_{re}\mathbf{K}_i+\mathbf{k}_i \text{ and } k_{hi}=m_{rh}\mathbf{K}_i-\mathbf{k}_i \quad \text{(D.6)}$$

which are derived using the additional relationship

$$m_{re}+m_{rh}=\frac{m_e}{M}+\frac{m_h}{M}=\frac{M}{M}=1.$$

The derivation of D.6 goes as follows. From equation D.3 we get

$$\begin{aligned} k_{ci} &= \mathbf{K}_i - k_{hi} \\ m_{re}k_{ei} &= m_{re}\left(\mathbf{K}_i - k_{hi}\right) \\ &= m_{re}\mathbf{K}_i - m_{re}k_{hi} + m_{rh}k_{ei} - m_{rh}k_{ei} \\ &= m_{re}\mathbf{K}_i + \mathbf{k}_i - m_{rh}k_{ei} \\ k_{ei}\left(m_{re} + m_{rh}\right) &= m_{re}\mathbf{K}_i + \mathbf{k}_i \\ k_{ei} &= m_{re}\mathbf{K}_i + \mathbf{k}_i \end{aligned}$$

and similarly for k_{hi}.

The exchange term $B^{\dagger}_{kh1,ke2-q}B^{\dagger}_{kh2,ke1+q}B_{kh2,ke2}B_{kh1,ke1}$ is converted by specifying

$$K_1 \rightarrow k_{e2} - q + k_{h1}$$

equations D.6 are then used to substitute for k_{e2} and k_{h1} gives

$$K_1 \rightarrow m_{re}\mathbf{K}_2 + \mathbf{k}_2 - q + m_{rh}\mathbf{K}_1 - \mathbf{k}_1$$

remembering that $m_{rh} = 1 - m_{re}$ gives

$$K_1 \rightarrow m_{re}\left(\mathbf{K}_2 - \mathbf{K}_1\right) + \mathbf{k}_2 - \mathbf{k}_1 + \mathbf{K}_1 - q.$$

We define

$$\mathbf{k}_{21} \equiv m_{re}\left(\mathbf{K}_2 - \mathbf{K}_1\right) + \mathbf{k}_2 - \mathbf{k}_1$$

and

$$\mathbf{K}_{E1} \equiv \mathbf{k}_{21} + \mathbf{K}_1$$

therefore

$$\mathbf{K}_1 = \mathbf{K}_{E1} - q.$$

Using a similar method we see that

$$\begin{aligned} k_1 &\rightarrow m_{rh}\left(k_{e2} - q\right) - m_{re}k_{h1} \\ &\rightarrow m_{rh}k_{e2} - m_{re}k_{h1} - m_{rh}q \end{aligned}$$

the substitution of equations D.6 gives

$$\begin{aligned} k_1 &\rightarrow m_{rh}\left(\mathbf{k}_2 + m_{re}\mathbf{K}_2\right) - m_{re}\left(m_{rh}\mathbf{K}_1 - \mathbf{k}_1\right) - m_{rh}q \\ &\rightarrow m_{rh}m_{re}\left(\mathbf{K}_2 - \mathbf{K}_1\right) + m_{re}\mathbf{k}_1 + m_{rh}\mathbf{k}_2 - m_{rh}q \\ &\rightarrow \mathbf{k}_1 + m_{rh}\left[m_{re}\left(\mathbf{K}_2 - \mathbf{K}_1\right) + \mathbf{k}_2 - \mathbf{k}_1\right] - m_{rh}q \\ &\rightarrow \mathbf{k}_1 + \mathbf{k}_{21} - m_{rh}q. \end{aligned}$$

We define

$$\mathbf{k}_{E1} \equiv \mathbf{k}_1 + \mathbf{k}_{21}$$

therefore

$$\mathbf{k}_1 \rightarrow \mathbf{k}_{E1} - m_{rh}q.$$

Similarly we find

$$\mathbf{K}_2 = \mathbf{K}_{E2} + q$$

where

$$\mathbf{K}_{E2} = \mathbf{K}_2 - \mathbf{k}_{21} \text{ and } \mathbf{k}_{E2} = \mathbf{k}_2 - m_{rh}\mathbf{k}_{21}$$

This give

$$B^{\dagger}_{kh1,ke2-q}B^{\dagger}_{kh2,ke1+q}B_{kh2,ke2}B_{kh1,ke1} = B^{\dagger}_{\mathbf{k}_{E1}-m_{rh}q,\mathbf{K}_{E1}-q}B^{\dagger}_{\mathbf{k}_{E2}+m_{rh}q,\mathbf{K}_{E2}+q}B_{\mathbf{k}_2}B_{\mathbf{k}_1}.$$

Through a similar procedure we find that

$$B^{\dagger}_{kh2-q,ke1}B^{\dagger}_{kh1+q,ke2}B_{kh2,ke2}B_{kh1,ke1} = B^{\dagger}_{\mathbf{k}_{E2}+m_{re}q,\mathbf{K}_{E2}-q}B^{\dagger}_{\mathbf{k}_{E1}-m_{re}q,\mathbf{K}_{E1}+q}B_{\mathbf{k}_2}B_{\mathbf{k}_1}$$

$$B^{\dagger}_{kh1,ke2+q}B^{\dagger}_{kh2-q,ke1}B_{kh2,ke2}B_{kh1,ke1} = B^{\dagger}_{\mathbf{k}_{E1}+m_{rh}q,\mathbf{K}_{E1}+q}B^{\dagger}_{\mathbf{k}_{E2}+m_{re}q,\mathbf{K}_{E2}-q}B_{\mathbf{k}_2}B_{\mathbf{k}_1}$$

and finally

$$B^{\dagger}_{kh2-q,ke1+q}B^{\dagger}_{kh1,ke2}B_{kh2,ke2}B_{kh1,ke1} = B^{\dagger}_{\mathbf{k}_{E2}+q,\mathbf{K}_{E2}}B^{\dagger}_{\mathbf{k}_{E1},\mathbf{K}_{E1}}B_{\mathbf{k}_2}B_{\mathbf{k}_1}.$$

E. Appendix E.

Transformation of the Hamiltonian to Exciton Basis.

Transformations to the exciton basis use the Fourier transform relation

$$B^{\dagger}_{\mathbf{k},\mathbf{K}} = \sum_{n} \Psi^{*}_{n,\mathbf{k}}B^{\dagger}_{n,\mathbf{K}}. \tag{E.7}$$

The first term

$$H_o = \sum_{k1,K1}\left(E^{o}_{\mathbf{k1},\mathbf{K1}}B^{\dagger}_{\mathbf{k1},\mathbf{K1}} - \sum_{\mathbf{q}} V_{\mathbf{q}}B^{\dagger}_{\mathbf{k1}+\mathbf{q},\mathbf{K1}}\right)B_{\mathbf{k1},\mathbf{K1}}$$

is the trickiest to transform. Substituting equation E.7 we get

$$\begin{aligned} H_o &= \sum_{\substack{k1,K1\\ n1,n2}}\left(E^{o}_{\mathbf{k1},\mathbf{K1}}\Psi^{*}_{n1,\mathbf{k1}}B^{\dagger}_{n1,\mathbf{K1}} - \sum_{\mathbf{q}} V_{\mathbf{q}}\Psi^{*}_{n1,\mathbf{k1}+\mathbf{q}}B^{\dagger}_{n1,\mathbf{K1}}\right)\Psi_{n2,\mathbf{k1}}B_{n2,\mathbf{K1}} \\ &= \sum_{\substack{k1,K1\\ n1,n2}}\left(E^{o}_{\mathbf{k1},\mathbf{K1}}\Psi^{*}_{n1,\mathbf{k1}} - \sum_{\mathbf{q}} V_{\mathbf{q}}\Psi^{*}_{n1,\mathbf{k1}+\mathbf{q}}\right)\Psi_{n2,\mathbf{k1}}B^{\dagger}_{n1,\mathbf{K1}}B_{n2,\mathbf{K1}} \end{aligned} \tag{E.8}$$

We know that $E^o_{\mathbf{k1,K1}}$ includes the energy of the gap term E_g. So we define $E^o_{\mathbf{k1,K1}} = E^o_{\mathbf{k1}} + E^o_{\mathbf{K1}} + E_g$; the energy connected with the relative motion, center of mass energy (E_{com}) and energy of the gap respectively. Dealing with the relative motion term first and remembering that

$$H_o \Psi_n = E^o_n \Psi_n \tag{E.9}$$

we get

$$\begin{aligned} \sum_{k2} H_{\mathbf{k1,k2}} \Psi^*_{n,\mathbf{k2}} &\equiv \sum_{k2} \left(E^o_{\mathbf{k1}} \delta_{\mathbf{k1,k2}} - \sum_{\mathbf{q}} V_{\mathbf{q}} \delta_{\mathbf{k1+q,k2}} \right) \Psi^*_{n,\mathbf{k2}} \\ &= E^o_{\mathbf{k1}} \Psi^*_{n,\mathbf{k1}} - \sum_{\mathbf{q}} V_{\mathbf{q}} \Psi^*_{n,\mathbf{k1+q}} \end{aligned}$$

then by equation E.9

$$\sum_{k2} H_{\mathbf{k1,k2}} \Psi^*_{n,\mathbf{k2}} = E^o_n \delta_{\mathbf{k1,k2}} \Psi^*_{n,\mathbf{k2}}$$

Thus equation E.8 can be written as

$$\begin{aligned} H_o &= \sum_{\substack{\mathbf{k1,K1,k2} \\ n1,n2}} \left(E^o_{n1} \delta_{\mathbf{k1,k2}} \Psi^*_{n1,\mathbf{k2}} \right) \Psi_{n2,\mathbf{k1}} B^\dagger_{n1,\mathbf{K1}} B_{n2,\mathbf{K1}} + (E_{com} + E_g) \text{ terms} \\ &= \sum_{\mathbf{K1},n1} E^o_{n1} B^\dagger_{n1,\mathbf{K1}} B_{n1,\mathbf{K1}} + (E_{com} + E_g) \text{ terms} \end{aligned} \tag{E.10}$$

since

$$\sum_{\mathbf{k1,k2}} \delta_{\mathbf{k1,k2}} \Psi^*_{n1,\mathbf{k2}} \Psi_{n2,\mathbf{k1}} = \delta_{n1,n2}. \tag{E.11}$$

The center of mass and energy gap terms will give

$$\sum_{\substack{k1,K1 \\ n1,n2}} (E^o_{\mathbf{K1}} + E_g) \Psi^*_{n1,\mathbf{k1}} \Psi_{n2,\mathbf{k1}} B^\dagger_{n1,\mathbf{K1}} B_{n2,\mathbf{K1}}$$

$$
\begin{aligned}
&= \sum_{\substack{K1 \\ n1,n2}} (E^o_{\mathbf{K1}} + E_g) \sum_{k1} \Psi^*_{n1,\mathbf{k1}} \Psi_{n2,\mathbf{k1}} B^\dagger_{n1,\mathbf{K1}} B_{n2,\mathbf{K1}} \\
&= \sum_{\substack{K1 \\ n1,n2}} (E^o_{\mathbf{K1}} + E_g)\, \delta_{n1,n2} B^\dagger_{n1,\mathbf{K1}} B_{n2,\mathbf{K1}} \\
&= \sum_{\mathbf{K1},n1} (E^o_{\mathbf{K1}} + E_g)\, B^\dagger_{n1,\mathbf{K1}} B_{n1,\mathbf{K1}}.
\end{aligned}
$$

Thus

$$
H_o = \sum_{\mathbf{k1},\mathbf{K1}} \left(E^o_{\mathbf{k1},\mathbf{K1}} B^\dagger_{\mathbf{k1},\mathbf{K1}} - \sum_{\mathbf{q}} V_{\mathbf{q}} B^\dagger_{\mathbf{k1}+\mathbf{q},\mathbf{K1}} \right) B_{\mathbf{k1},\mathbf{K1}} \rightarrow \sum_{v1} E^o_{v1} B^\dagger_{v1} B_{v1}
$$

where

$$
E^o_{v1} \equiv E^o_{n1} + E^o_{\mathbf{K1}} + E_g = E^o_{n1} + \frac{\hbar^2 K^2}{2M} + E_g.
$$

The other terms are all straight forward conversions, a sample direct term is

$$
\begin{aligned}
&\sum_{\mathbf{k}_1\mathbf{k}_2} V_q B^\dagger_{\mathbf{k}_1 - m_{re}q, \mathbf{K}_1+q} B^\dagger_{\mathbf{k}_2+m_{re}q, \mathbf{K}_1-q} B_{k2} B_{k1} \\
&= \sum_{\mathbf{k}_1\mathbf{k}_2} \sum_{\substack{n,n2 \\ n3,n4}} V_q \Psi^*_{n,\mathbf{k}_1 - m_{re}q} B^\dagger_{n,\mathbf{K}_1+q} \Psi^*_{n2,\mathbf{k}_2+m_{re}q} B^\dagger_{n2,\mathbf{K}_1-q} \Psi_{n3,\mathbf{k}2} B_{n3,\mathbf{K}2} \Psi_{n4,\mathbf{k}1} B_{n4,\mathbf{K}1} \\
&= \sum_{\mathbf{k}_1\mathbf{k}_2} \sum_{\substack{n,n2 \\ n3,n4}} V_q \left(\Psi^*_{n,\mathbf{k}_1 - m_{re}q} \Psi^*_{n2,\mathbf{k}_2+m_{re}q} \Psi_{n3,\mathbf{k}2} \Psi_{n4,\mathbf{k}1} \right) B^\dagger_{n,\mathbf{K}_1+q} B^\dagger_{n2,\mathbf{K}_1-q} B_{n3,\mathbf{K}2} B_{n4,\mathbf{K}1} \\
&= \sum_{v1,v2} W^{n,n2}_{n3,n4} B^\dagger_{n,\mathbf{K}_1+q} B^\dagger_{n2,\mathbf{K}_1-q} B_{v2} B_{v1}.
\end{aligned}
$$

The other direct and exchange terms are found in a similar manner as is the field term.

Bibliography

[1] Jacobson J.,Cao H.,Björk G., Pau S., and Yamamoto Y., *Extended Abstracts of the 1994 International Conference on Solid State Devices and Materials*, 133-135 (1994).

[2] Fortin E., Fafard S. and Mysyrowicz A., *Phys. Rev. Let.* Vol. **70 # 25**, 3951 (1993). Benson E., Fortin E. and Mysyrowicz A., *Phys. Stat. Sol.* **191**, 345 (1995). Mysyrowicz A., Benson E. and Fortin E., *Phys. Rev Let.* Vol. **77 # 5**, 896 (1996).

[3] Iguchi K., *Phys. Rev Let.* Vol. **78 # 17**, 3233 (1997).

[4] Usui T., *Progress of Theoretical Physics* Vol. **23 # 5**, 787 (1960).

[5] Sawada K., *Phys. Rev* Vol. **106 # 2**, 372 (1956).

[6] Wentzel G., *Phys. Rev* Vol. **108 # 6**, 372 (1957).

[7] Hanamura E. and Haug H., *Phys. Report, Sec. C of Phys. Let.* Vol. **33 # 4**, 209 (1977).

[8] Haug H. and Koch S. W., *Quantum Theory of the Optical and Electronic Properties of Semiconductors* (World Scientific, Singapore, 1994) 3rd Ed..

[9] Bassani F., Ruggiero F. and Quattropani A., *IL Nouvo Cimento* Vol. **7D** # **5**, 701 (1986).

[10] Greenberg O. W., *Phys. Rev. D* Vol. **43** # **12**, 4111 (1991).

[11] Axt V.M., Bartels G. and Stahl A., *Phys. Rev. Let.* Vol. **76** # **14**, 2543 (1996). Axt V.M. and Stahl A., *Z. Phys. B* **93**, 195 (1994).

[12] Klingshirn C.F., *Semiconductor Optics* (Springer, Germany, 1995).

[13] Knox R.S., *Theory of Excitons, Solid State Physics Supplement 5* (Academic Press, U.S.A., 1963).

[14] Dextor D.L. and Knox R.S., *Excitons* (Interscience Publishers, New York, 1965).

[15] Ziman J.M., *Elements of Advanced Quantum Theory* (Cambridge University Press, U.K., 1969).

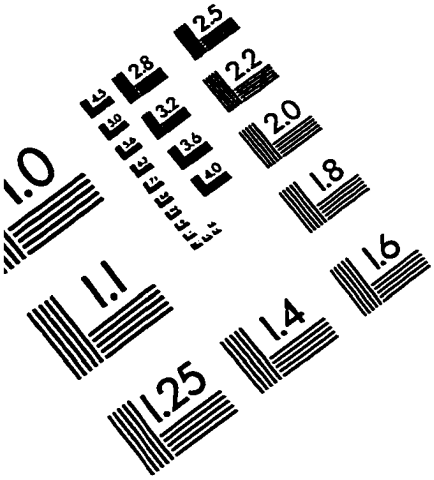
[16] Goswami A., *Quantum Mechanics* (Wm. C. Brown Pub., U.S.A., 1992).

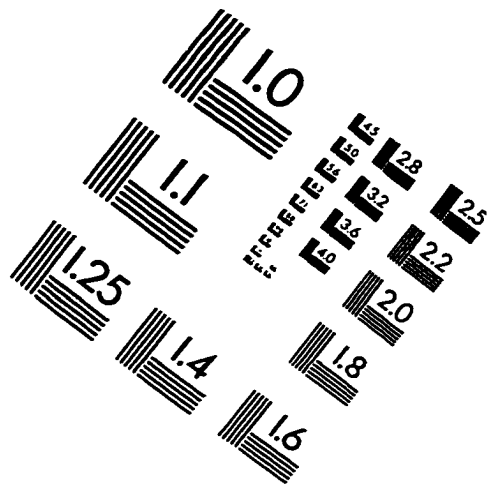
[17] Jackson J. D., *Classical Electrodynamics* (John Wiley & Sons, U.S.A, 1975) 62nd Ed..

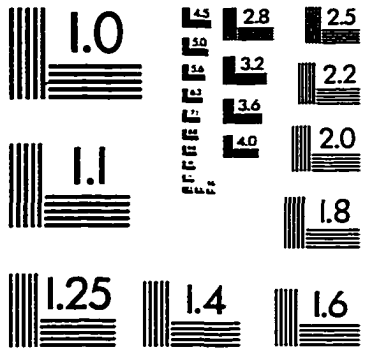
[18] Kittel C., *Introduction to Solid State Physics* (John Wiley & Sons, U.S.A, 1986) 6th Ed..

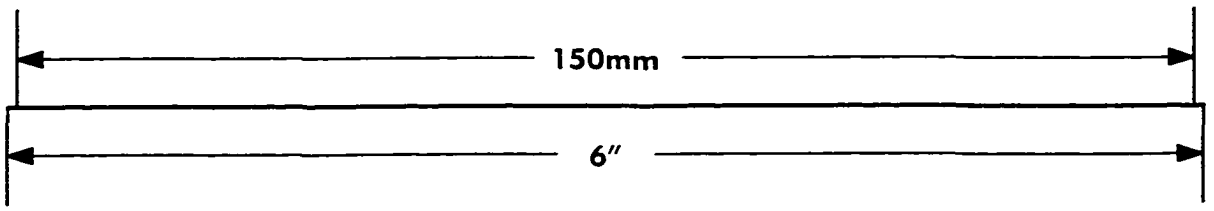
[19] Hawton M. and Nelson D., *To be published in Phys. Rev. B* (Lakehead University, Canada, 1997).

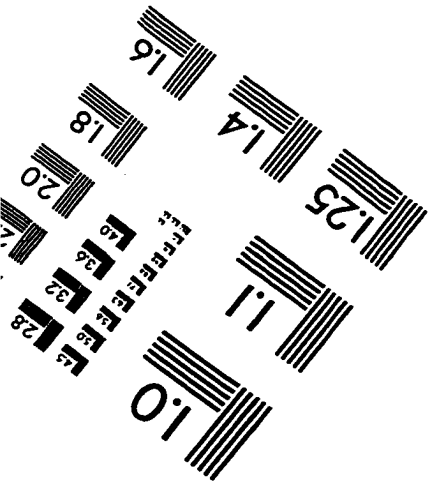
IMAGE EVALUATION TEST TARGET (QA-3)

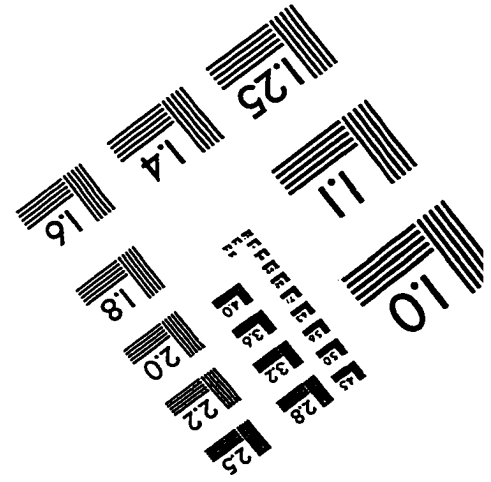












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